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Fabrication and Actuation of Hierarchically-Patterned Polymer Substrates for Dynamic Surface and Optical Properties

Abstract

Switchable optical materials, which possess reversible color and transparency change in response to external stimuli, are of wide interest for potential applications such as windows and skylights in architectural and vehicular settings or optical sensors for environmental monitoring. This thesis considers the tuning of optical properties by tailoring and actuating responsive materials. Specifically, we demonstrate the design and fabrication of tilted pillar arrays on wrinkled elastomeric polydimethylsiloxane (PDMS) as a reversibly switchable optical window. While the original PDMS film exhibits angle-dependent colorful reflection due to Bragg diffraction of light from the periodic pillar array, the tilted pillar film appears opaque due to random scattering. Upon re-stretching the film to the original pre-strain, the grating color is restored due to the straightened pillars and transmittance is recovered. Then, we develop a composite film, consisting of a thin layer of quasi-amorphous array of silica nanoparticles (NPs) embedded in bulk elastomeric PDMS, with initial high transparency and angle-independent coloring upon mechanical stretching. The color can be tuned by the silica NP size. The switch between transparency and colored states could be reversibly cycled at least 1000 times without losing the film's structural and optical integrity.

We then consider the micropatterning of nematic liquid crystal elastomers (NLCEs) as micro-actuator materials. Planar surface anchoring of liquid crystal (LC) monomers is achieved with a poly(2-hydroxyethyl methacrylate)-coated PDMS mold, leading to monodomains of vertically aligned LC monomers within the mold. After cross-linking, the resulting NLCE micropillars show a relatively large radial strain when heated above nematic to isotropic transition temperature, which can be recovered upon cooling. Finally, the understanding of liquid crystal surface anchoring under confined boundary conditions is applied to the self-assembly of gold nanorods (AuNRs) driven by LC defect structures and to dynamically tune the surface plasmon resonance (SPR) properties. By exploiting the confinement of the smectic liquid crystal, 4-octyl-4'-cyanobiphenyl (8CB), to patterned pillars treated with homeotropic surface anchoring, topological defects are formed at precise locations around each pillar and can be tuned by varying the aspect ratio of the pillars and the temperature of the system. As a result, the AuNR assemblies and SPR properties can be altered reversibly by heating and cooling between smectic, nematic and isotropic phases.

Degree Type Dissertation

Degree Name Doctor of Philosophy (PhD)

Graduate Group Materials Science & Engineering

First Advisor Shu Yang

Keywords

actuation, elastomer, liquid crystal assembly, smart window, structural color, tunable optical properties

Subject Categories Mechanics of Materials

FABRICATION AND ACTUATION OF HIERARCHICALLY-

PATTERNED POLYMER SUBSTRATES FOR DYNAMIC

SURFACE AND OPTICAL PROPERTIES

Elaine Lee

A DISSERTATION

in

Materials Science and Engineering

Presented to the Faculties of the University of Pennsylvania

in

Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

2015

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ACKNOWLEDGEMENTS

A PhD dissertation is never a lone effort and I could not have come this far without the love and assistance of the people around me. I am truly grateful for the invaluable input and support of my professors, collaborators, colleagues, friends and family, without which this dissertation could not have been possible.

First and foremost, I would like to sincerely express my gratitude and appreciation to my advisor, Professor Shu Yang. She has dedicated so much of her time and effort to support her group in our scientific exploration as well as our writing and presentation skills. Her breadth of knowledge and courage in pursuing research outside her core expertise through ambitious collaborations has truly motivated me throughout my graduate years and will continue to inspire me through my career.

I would like to thank my committee members, Professor Russell Composto of the Department of Materials Science and Engineering, Professors Daeyeon Lee and Kathleen Stebe of the Department of Chemical and Biomolecular Engineering, and Professor Jason Burdick of the Department of Bioengineering, for supporting me throughout my graduate studies with advice and suggestions for my research.

I am grateful to all my collaborators for sharing their knowledge in other fields and inspiring novel directions for my projects. Professor Nader Engheta, Professor Jan van der Spiegel, Dr. Milin Zhang, and Hongjie Zhu of the Department of Electrical and Systems Engineering and Professor Jenny Sabin and Andrew Lucia of the Department of Architecture, Art, and Planning at Cornell University provided tremendous insights for the smart window projects through our monthly EFRI-SEED meetings and crossdepartmental experiments. Professors Daniel Gianola and Ertugrul Cubukcu provided instrumentation for the characterization of smart windows. I would like to express gratitude to Professor Kaori Ihida-Stansbury and Mithil Chokshi of the Department of Pathology and Laboratory Medicine and Professor Kahp Yang Suh, Laura Ha, and Kim Min-sung of Seoul National University for providing experimental training and support for cell biology studies. Professor Yaling Liu and Shunqiang Wang of Lehigh University introduced me to a completely different field of research through our collaborative work on circulating tumor cell capture using herringbone microfluidic devices.

Professor Russell Composto and Robert Ferrier provided materials and support, while Professor Kathleen Stebe of the Department of Chemical and Biomolecular Engineering and Professor Randall Kamien and Dr. Daniel Beller of the Department of Physics and Astronomy provided theoretical insights and inspiration for the gold nanorod/liquid crystal studies. Professor Rudolf Zentel and Dr. Eva-Kristina Fleischmann of the Johannes Gutenberg-Universität Mainz provided initial materials and training which inspired the micro-scale liquid crystal elastomer project.

I would like to express my appreciation of the members of the Yang group, past and present, for their creative input and assistance throughout my research, including Dr. Chi-mon Chen, Dr. Yigil Cho, Dr. Younghyun Cho, Dr. Dengteng Ge, Dr. Mohamed Amine Gharbi, Dr. Apiradee Honglawan, Euiyeon Jung, Hye-Na Kim, Dr. Su Yeon Lee, Dr. Jie Li, Zhiwei Liao, Dr. Yudi Rahmawan, Dr. Francesca Serra, Luke Shi, Chenbo Wang, Gaoxiang Wu, Yu Xia, Dr. Lebo Xu, Professor Lili Yang, Professor Youfa Zhang, and Yongwei Zheng.

I would like to express appreciation to Dr. Jamie Ford, Dr. Matthew Brukman, Steve Szewczyk, Kyle Keenan, Hiromichi Yamamoto, and Eric Johnston for training and assistance on instrumentation and characterization. I would also like to thank Patricia Overend, Vicky Lee, Irene Clements, Raymond Hsiao and Enrique Vargas for their dayto-day support in making my life easier in the department.

I would like to recognize the other MSE students, past and present, for our shared adventures and shenanigans throughout the years, including Daksh Agarwal, Dr. Carlos Aspetti, Jacob Berger, Dr. Lisa Chen, Dr. Vicky Doan-Nguyen, Nicholas Greybush, Dr. David Kim, Daniel Magagnosc, L. Robert Middleton, Dr. Kathryn Muphy, Dr. Rose Mutiso, Dr. Pavan Nukala, Dr. Michael O'Reilly, Emmabeth Parrish, Boris Rasin, Frank Streller, Daniel Strickland, Spencer Thomas, Edward Trigg, Han Chang Yang, and Hai Zhu.

I am especially thankful for the MSE PhD students of my year, including Rahul Agarwal, E. Ashley Gaulding, Jiechang Hou, Chia-Chun Lin, Joohee Park, Jason Reed, Sharon Sharick, Dr. Wei-Shao Tung, and Ryan Wade. They have been through it all with me: first year classes, qualifying exams, weddings in India, research proposals, happy hours, paper writing, hurricanes, snow days, and thesis writing. I am fortunate to have come through this journey with them and have truly enjoyed our times together.

Finally, I would like to dedicate my thesis to my parents, Hong Bo Lee and Shao Yun Wu, and my sisters, Sarah and Alicia Lee, for their unconditional love and sacrifice. My parents, who grew up without education, have lived and worked relentlessly their whole lives to afford me all the opportunities they could not have. They left their homes and families half a world behind for uncertain prospects of a better future for my sisters and me. My sisters' tough love and carefree vivacity remind me to be true to myself and remain young at heart.

ABSTRACT

FABRICATION AND ACTUATION OF HIERARCHICALLY-PATTERNED POLYMER SUBSTRATES FOR DYNAMIC SURFACE AND OPTICAL PROPERTIES

Elaine Lee

Shu Yang

Switchable optical materials, which possess reversible color and transparency change in response to external stimuli, are of wide interest for potential applications such as windows and skylights in architectural and vehicular settings or optical sensors for environmental monitoring. This thesis considers the tuning of optical properties by tailoring and actuating responsive materials. Specifically, we demonstrate the design and fabrication of tilted pillar arrays on wrinkled elastomeric polydimethylsiloxane (PDMS) as a reversibly switchable optical window. While the original PDMS film exhibits angle-dependent colorful reflection due to Bragg diffraction of light from the periodic pillar array, the tilted pillar film appears opaque due to random scattering. Upon re-stretching the film to the original prestrain, the grating color is restored due to the straightened pillars and transmittance is recovered. Then, we develop a composite film, consisting of a thin layer of quasi-amorphous array of silica nanoparticles (NPs) embedded in bulk elastomeric PDMS, with initial high transparency and angle-independent coloring upon mechanical stretching. The color can be tuned by the silica NP size. The switch between transparency and colored states could be reversibly cycled at least 1000 times without losing the film's structural and optical integrity.

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CHAPTER 1: Bio-inspired design of tunable optical properties for smart window and sensor applications

Adapted from:

Ge, D.,[†] Lee, E.,[†] Yang, L., Cho, Y., Li, M., Gianola, D. S. and Yang, S. (2015), A Robust Smart Window: Reversibly Switching from High Transparency to Angle-Independent Structural Color Display. Adv. Mater., 27: 2489–2495. [†]Equal Contribution.¹ Reproduced with permission.

Lee, E. and Yang, S. "Bio-inspired Responsive Polymer Pillar Arrays." MRS Commun., 2015, doi:10.1557/mrc.2015.18. (Invited Perspective on Polymers/Soft Matter)²

1.1 Introduction

The manipulation of nano- and microscaled surface features offers a wellcontrolled approach for modulating optical phenomena. In nature, there is an abundance of hierarchical patterns which offer multi-scale functionality and tunability, such as the self-cleaning and hydrophobic lotus leaf,³⁻⁵ the chemically-sensitive structural color of the *Morpho* butterfly,⁶⁻⁸ and the adhesion pad of gecko lizards.⁹⁻¹¹ These properties arise from the micro- and nanostructures of the systems. Advances in micro- and nanofabrication techniques have allowed for the fabrication of multi-scale hierarchical structures with dynamic properties. Physical modification, through the combination of bottom-up self-assembly and top-down lithography techniques, is a simple and wellcontrolled approach to fabricate artificial multi-functional and well-ordered surfaces.¹²⁻¹⁵ By drawing inspiration from naturally occurring structural color and exploiting the responsiveness of polymer systems, the fabrication and actuation of multi-scale, dynamically-tunable optical components can be realized. Here, structural color, their underlying optical properties and examples of structural color in nature are introduced. The fabrication of artificial color using responsive materials, with an emphasis on elastomers and liquid crystals, and the manipulation of these systems are discussed.

1.2 Optical origins of structural color

The perception of color comes from interplay between the light source, the objects that interact with light, and the detector of light. The wavelength of light detected defines the color observed and new colors can be achieved by additive or subtractive color mixing. Additive coloring is created by mixing light of different wavelengths while subtractive coloring is created by selectively absorbing specific wavelengths of light using dyes, inks, pigments or filters.¹⁶ If all wavelengths of light are reflected, absorbed or transmitted, white, black or transparency is observed, respectively. Structural color results from the physical interaction of light with structures with length scales on the order of the wavelength of light. They are typically brighter and shinier than pigment colors, which can fade away over time under the sun. Structural color can be defined by the following optical processes and their combinations: thin-film interference, multi-layer interference, diffraction grating, and light scattering (**Figure 1.1**).¹⁷⁻¹⁹



Figure 1.1 Schematic diagram of (a) thin-film interference, (b) multi-layer inference, (c) diffraction, and (d) left to right: 1D, 2D, and 3D photonic crystals.

1.2.1 Thin-film interference

When a plane wave of light strikes a thin layer of thickness d and refractive index n_2 at an angle θ_1 , the light is reflected at the top interface with air, refracted at an angle of θ_2 , and reflected at the bottom interface of the layer. The reflected beams from the two interfaces interfere with each other. Constructive interference, such that reflection is enforced, occurs when light of wavelength λ meets the following condition:

$$2n_2d\cos\theta_2 = m\lambda\tag{1-1}$$

where m is an integer when the thin layer is attached to a material with higher refractive index, e.g. anti-reflective coatings, and a half integer when it is not, e.g. soap bubbles. The wavelength of maximum reflectivity is given by:

$$\lambda_{max} = \left(\frac{4n_2d}{2m+1}\right)^2 \left(1 - \frac{n_1^2}{n_2^2} \sin^2 \theta_1\right)^4 \tag{1-2}$$

As the incident angle increases, the wavelength of maximum reflectivity decreases, i.e. the color is angle-dependent, a phenomenon known as iridescence.

1.2.2 Multi-layer interference

Multi-layer interference occurs when two or more thin layers of different refractive indices are stacked. Considering two layers, A and B, with thicknesses $d_A > d_B$ and refractive indices n_A and n_B stacked periodically on top of each other, the relation for constructive inference for an anti-reflective coating (i.e. the phases of the reflected light at the upper and lower interfaces between B and A change by 180°) is:

$$2(n_A d_A \cos \theta_A + n_B d_B \cos \theta_B) = m\lambda \tag{1-3}$$

where θ_A and θ_B are the angles of refraction of layers A and B, respectively. If the phase of the reflected light does not change at the A-B interface, then the following is also satisfied:

$$2n_A d_A \cos \theta_A = \left(m' + \frac{1}{2}\right)\lambda \tag{1-4}$$

The reflection at the interface adds to the interference, giving maximum reflectivity when m' < m. The wavelength at which first-order maximum constructive interference occurs $\lambda_{max} = 2(n_A d_A + n_B d_B)$ for any multi-layer. For the ideal multi-layer (i.e. m = 1 and m' = 0), the optical path lengths are equal, $n_A d_A = n_B d_B = \lambda_{max}/4$, and the light reflected from every interface interferes constructively. If the thickness of layer A does not satisfy Equation (1-4), but the sum of layers A and B $(n_A d_A + n_B d_B)$ satisfies Equation (1-3), then the reflection at the A-B interface is destructively interfering and the peak reflectivity can be decreased, i.e. the non-ideal multi-layer.

1.2.3 Diffraction grating

A diffraction grating is an optical component with periodic structures with lengths on the order of the wavelengths of light that split and diffract light into different directions, resulting in color. The diffracted light is the sum of the interfering light beams from each slit. The phase of the beams varies since the optical path length varies from each slit, resulting in constructive and destructive interference. When a plane wave of light is normally incident on a diffraction grating with slits of spacing *d*, the diffracted light has maxima at angles θ_m given by:

$$d\sin\theta_m = m\lambda \tag{1-5}$$

where m is the order of the diffracted beam.

1.2.4 Photonic crystals

Photonic crystals are materials that have periodically-modulated indices of refraction in one, two, or three dimensions, where light are interfered and totally reflected at the surface of the crystals at specific wavelengths, i.e. a photonic band gap (PBG). The location and width of the PBGs is determined by photonic crystal structures, including the symmetry, periodicity, volume filling fraction (or porosity), and refractive index contrast between the high and low dielectric materials.²⁰ Here, we are primarily concerned with the resultant color. The color of photonic crystals arises from interference of reflected light as described by Bragg-Snell's law:

$$\lambda = 2d(n_{eff}^2 - \cos^2 \theta)^{1/2}$$
(1-6)

where d is the lattice spacing, n_{eff} is the average refractive index of the constituent materials, θ is the incident angle of light.

1.2.5 Light scattering

Unlike other structural color, the color generated by light scattering arises from structural irregularity. The scattering of electromagnetic radiation, i.e. broadband or Mie scattering, from a sphere is given by the Mie solution in the form of an infinite series of spherical Bessel functions.²¹ In the case of Rayleigh scattering, the intensity of unpolarized radiation of wavelength λ and intensity I_0 scattered from a particle much smaller than the wavelength of light is given by:

$$I' = I_0 \frac{1 + \cos^2 \theta}{2R^2} \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{D}{2}\right)^6$$
(1-7)

where θ is the scattering angle, *R* is the distance between the particle and the detector, *n* is the index of refraction of the particle, and *D* is the diameter of the particle. For a particle film, the intensity is given by:

$$\frac{I}{I_0} = \frac{NI'}{I_0} \tag{1-8}$$

where *N* is the number of particles per unit volume.

1.3 Natural and artificial structural colors

Biological organisms use color for a number of purposes, including signaling, camouflage, mating display, and optical filtering. Nature has evolved a multitude of structures, ranging from one-dimensional (1D) gratings to two-dimensional (2D) multi-layers to three-dimensional (3D) photonic crystals, which exhibit structural color derived from a combination of the processes described above.^{6,8,19,22-25} Structural color can be divided into two classes: angle-dependent color from coherent interference and/or diffraction on periodic structures, as seen in some butterfly wings and beetle scales, ^{17,19,25} and angle-independent color from scattering on quasi-amorphous structures, as seen in some bird feathers and mandrill skin.²⁶ Among the many organisms exhibiting structural color, the most widely studied is the *Morpho* butterfly.^{6-8,17} Male *Morpho* butterfly wings appear shiny blue, resulting from multi-layer interference within the hierarchical ridge/lamellar structure. Irregularity in the heights of the narrow ridges cancels the

interference between neighboring ridges, resulting in wide-angle reflection. In addition, pigments underneath the structure absorb unnecessary colors to enhance the color contrast. It is notable that the brilliant iridescent color observed results from a combination of structure regularity, irregularity, and pigmentation.

While brilliant color is aesthetically pleasing, switchable color and/or transparency to suit the local environment may be desired in organisms for signaling or mating purposes.^{24,27,28} For example, color changes are observed for *Morpho* butterfly wings in different vapors⁷ due to gas adsorption within the lamellae structures and for longhorn beetle scales at different levels of humidity²⁴ due to changes of refractive index in the surrounding medium. Color and transparency change are also advantageous for camouflage under stressful conditions. Hercules²⁹ and tortoise³⁰ beetles change color when under mechanical stress by effectively changing the difference in refractive indices within their structures via hydration and dehydration, allowing more and less light to be absorbed, respectively. Squids and octopi can switch between transparency and red color to become invisible to a predatory fish in down-welling light or to a predatory fish with bioluminescent searchlights, respectively, by stretching/contracting their skin to reveal/hide the embedded chromatophores.³¹⁻³³

Fabrication of artificial structures has been extensively studied to mimic the color and transparency changes found in nature. Often, polymeric materials are employed as the responsive components, either patterned at the optical scale or embedded with optical-scale particles. Given the immense library of available constituents, the composition, functional groups, architecture, and multi-scale morphology of polymeric materials can be tuned to induce dramatic and often reversible changes in shape,³⁴ volume,³⁵ morphology,³⁶ and mechanical³⁷ and optical properties.^{38,39} By engineering specific responsiveness, controlled transitions can be achieved, resulting in changes to the feature size, spacing, and refractive index and thus to the optical properties. Polymeric materials that are responsive to external stimuli, including temperature, pressure, pH, light, and electric and magnetic fields, are of interest for a wide variety of applications. Stimuli responsiveness arises from a system's ability to transition between two minimum energy states when triggered either physically (i.e. mechanically, electrically, magnetically, optically, and thermally) or chemically (electrochemically, ionically, and biologically).^{2,13,15,40-47}

1.3.1 Hydrogels

Responsive polymers undergo conformational changes as a result of a change in the polymer chain interactions. While polymers readily respond to stimuli in solutions, polymers existing in other states of matter require greater energetic inputs for responsiveness due to their limited segmental motions, dimensional restrictions, and structural integrity. Common states of polymers include cross-linked gels, elastomers, and polymer solids. Stimuli-responsive gels are formed by chemically or physically cross-linking responsive polymers.⁴⁰ In particular, hydrophilic polymers can be cross-linked to form hydrogels which can swell in solvents, depending on temperature, pH and ionic strength.^{43,48,49} The responsiveness of hydrogels can be tuned by both the constituent polymers and their responsiveness, as well as by the cross-linking density and cross-linking distribution of the hydrogels. Gels can be glassy in the dry state but exhibit a significant drop in elastic modulus in the swollen state.

Thermo-responsive polymers often possess either a lower or upper critical solution temperature, at which they undergo a coil-to-globule transition or vice versa.⁴⁹ A well-known example is poly(N-isopropylacrylamide) (PNIPAAm), which has a lower critical solution temperature (LCST) above which it becomes hydrophobic and collapses out of water. By embedding a non-close-packed 3D colloidal crystal into a PNIPAAm hydrogel, thermally tunable diffraction was realized.⁵⁰ When the system is heated above the LCST, the hydrogel shrinks, thereby reducing the inter-particle distance and the diffraction wavelength. Alternatively, PNIPAAm nanogel particles have been selfassembled into colloidal crystals and polymerized, allowing thermally-induced synchronized shrinking of the particles. The change in the nanogel particle size and spacing results in increased diffraction and a drop of transmitted light within 900 ns. Porous thermo-sensitive hydrogels have also been fabricated by infiltrating a mixture of thermo-sensitive monomer and cross-linker into a colloidal crystal followed by gel crosslinking and colloidal template removal.^{51,52} The color of the gel can be controlled by either the dimensions of the colloidal crystal or by the concentration of the cross-linker. The diffraction spacing of the inverse-opal gels can then be tuned by controlling the temperature.

pH-responsive polymers have functional groups which are able to donate or accept protons under different pH conditions, which results in electrostatic repulsions between the resulting charges along the polymer backbone.⁴¹ Polyacids, such as poly(acrylic acid) (PAA), release protons and swell at pH values above their pKa. Contrarily, polybases such as poly(vinyl pyridine) (PVP) accept protons and swell at pH values below their pKa. Inverse opal hydrogels copolymerized with pH-sensitive functional groups enable pH-induced swelling and therefore color change.^{53,54} Alternatively, hydrogels can be functionalized with molecular-recognition groups for the selective binding of ions or molecules, leading to swelling-induced color change.⁵⁴⁻⁵⁷ Similarly, by incorporating photochromic molecules into hydrogels, optically-induced color change has been demonstrated.⁵⁸⁻⁶⁰ Common light-sensitive molecules include azobenzene, which undergoes a *cis-trans* isomerization; spiropyran, which ionizes and generates a dissociated ion pair; and cinnamate, which dimerizes and cross-links two molecules in response to UV irradiation.

1.3.2 Shape memory polymers

While hydrogels offer multi-stimuli responsiveness and versatility, swelling of hydrogels requires a solvent thereby limiting the practical application, especially at larger scales. Polymer solids are highly cross-linked polymer networks, which have limited mobility and low free volume, resulting in restricted stimuli-responsive behaviors. In order to improve responsiveness, it is common to copolymerize the responsive solid with lower glass transition segments or add fillers to plasticize the material and increase the free volume. Alternatively, the polymer networks can be designed with cross-links which can be reversibly broken upon triggering.⁶¹ Polymers which can be programmed with temporary shapes and subsequently recover their permanent shapes are known as shape memory polymers (SMPs).^{62,63} Most commonly, the shape change is thermally induced, whereupon heating the SMP above a transition temperature (T_{trans}) will decrease the Young's modulus by 2 or 3 orders of magnitude, allowing for the SMP to be deformed to a temporary shape. The temporary shape can then be fixed by cooling the sample.

Reheating SMP in the temporary shape to above T_{trans} triggers the relaxation of the stored elastic energy and the recovery of the permanent shape. Cooling again to below T_{trans} solidifies the permanent shape. The process can then be repeated to program a different temporary shape. By exploiting this property, the deformation of SMPs consisting of periodic microhole arrays⁶⁴ and micro-optic components⁶⁵ was demonstrated to switch between color and transparency.

1.3.3 Elastomers

Elastomers are polymer networks with low cross-linking density, allowing them to have high deformability even in the dry state. Polydimethylsiloxane (PDMS) is a typical elastomer that can be deformed mechanically due to its low elastic modulus, on the order of a few MPa.⁶⁶ PDMS is also advantageous for the fabrication of nano- and microscale features via soft lithography.⁶⁷ The reversible stretching of tapered PDMS nanopillar arrays (top diameter = 150 nm; bottom diameter = 300 nm; height = 150, 350, 700 nm) on a microwrinkled PDMS film (wavelength $\lambda = 31 \,\mu$ m, amplitude $A = 4.4 \,\mu$ m) has been reported for mechanically tunable wetting and transparency.²⁷ PDMS substrates pre-patterned with nanopillars were pre-stretched and treated with oxygen plasma to induce wrinkling. As fabricated, the substrates are opaque but become transparent with strain. The nanopillars render the substrates superhydrophobic. The switchable transmission (transparent \leftrightarrow opaque) is achieved primarily by reversibly flattening the microwrinkles while the nanopillars are rather transparent in the visible wavelength. Similar to other reports, a non-close-packed 3D colloidal crystal was embedded within

PDMS. The diffraction spacing was reduced upon mechanical stretching, resulting in a blue shift of the reflectance maximum of the film.⁶⁸

1.3.4 Liquid crystal elastomers

Liquid crystal elastomers (LCEs) are a unique class of shape memory elastomers, which combine the properties of liquid crystals (orientational order and responsiveness) and polymer networks (rubbery elasticity).⁶⁹⁻⁷³ The behavior of LCEs depends on their physical properties as defined by the liquid crystalline (LC) phases of the incorporated mesogens. LC phases exist at temperatures between the solid (crystalline) and liquid (isotropic melt) phases and are defined by the orientation of their anisotropic mesogens, represented by a dimensionless unit vector known as the local director *n* (Figure 1.2). Typically, LCs formed by rod-like molecules transition from the isotropic phase to the nematic phase to the smectic phase to the crystalline phase when cooled.



Figure 1.2 Schematic representation of the (a) isotropic, (b) nematic, cholesteric, (c) smectic A, and smectic C phases. The red arrows indicate the local director n and the green arrow indicates the layer normal of the smectic phases.

The isotropic phase is a disordered phase, where the LC molecules are oriented randomly. In nematic phases, LC molecules have long-range rotational order but no longrange translational order, such that their center-of-mass is randomly distributed but their
long axes are aligned roughly parallel to a local director axis (**Figure 1.2b**).⁶⁹ An order parameter can be used to define the average alignment of the LC molecules:

$$S = \frac{\langle 3\cos^2\theta - 1 \rangle}{2} \tag{1-9}$$

where θ is the angle between the long axis of the LC molecule and the local director. For complete random alignment, S = 0 and for perfect alignment, S = 1. Topological defects in LCs are places where the order parameter is undefined and small isotropic regions may be embedded in the LC phase. These defects can exist in the form of points and lines.⁷⁴ The winding number of a LC defect is defined by the angle that the local director turns on a loop around the defect divided by 2π . Typical defects found in nematic LCs are shown in **Figure 1.3**.



Figure 1.4 2D topological defects in nematic LCs. Point defects with winding number (a) -1/2, (b) +1/2, (c) -1, and (d) +1. (e) Line defect. Red lines define the local director and blue defines the defect.

Cholesteric LCs can be considered twisted nematic structures, with local in-plane nematic ordering but with a helical director distribution across the planes. The chiral pitch is defined by the distance over which the molecules rotate by 360°. Smectic LCs have quasi-long-range translational order (**Figure 1.2c**). Smectic LCs form parallel layers, in which the molecules are aligned with the local director parallel to or tilted from the layer normal with no long-range translational order within the layers, i.e. smectic A or smectic C phase, respectively.



Figure 1.5 Schematic representation of the surface anchoring of LC molecules.

When confined to a surface, LC molecules can be aligned by the topology, topography, and surface chemistry at the interface. Homeotropic and planar anchoring are defined as the alignment of LCs perpendicular and parallel to a surface, respectively (**Figure 1.4**). Depending on the boundary conditions of the nematic LCs, the director field may be distorted to accommodate the surface anchoring of the molecules via splay, twist, or bend elastic deformations (**Figure 1.6a-c**).⁷⁵ The Frank elastic free energy density describes the penalty for distortions of the director in nematic LCs:

$$F_{nematic} = \frac{1}{2} \Big[K_1 (\nabla \cdot n)^2 + K_2 \big(n \cdot (\nabla \times n) \big)^2 + K_3 \big(n \times (\nabla n) \big)^2 \Big]$$
(1-10)

where the K_1 , K_2 , and K_3 refer to the splay, twist, and bend curvature elastic constants, respectively. In the smectic phase, bend and twist of the director are prohibited (**Figure 1.6d**) and the free energy density depends on the splay, saddle-splay, and compressibility:

$$F_{smectic} = \frac{1}{2} K_1 \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \overline{K} \frac{1}{R_1 R_2} + \frac{1}{2} B \left(\frac{d - d_0}{d_0} \right)^2$$
(1-11)

where R_1 and R_2 are the principle radii of curvature of the layers, \overline{K} is the saddle-splay elastic constant, B is the compression modulus, and d and d_0 are the distorted and equilibrium layer thickness, respectively.



Figure 1.6 (a) Splay, (b) twist, and (c) bend deformations of nematic LCs. (d) Splay deformation of smectic LC. Reproduced with permission from reference 75.

LC monomers with functional groups can be cross-linked to form liquid crystalline polymers (LCPs) or LCEs. Due to the permanent dipoles in the polymer matrices of LCEs and the resulting optical and geometrical anisotropies, LCEs can respond to electromagnetic fields by realigning their mean optical axis parallel to the external field, resulting in orientation changes.⁷⁶ In addition, the orientational order of the mesogens can be controlled by temperature or solvent as well as light with the addition of photo-chromic molecules,⁷⁷ resulting in conformation and/or shape change.⁷² Nematic LCEs exhibit a reversible shape memory effect, i.e. the permanent shape can be recovered upon removal of the stimulus or with the application of an additional stimulus.⁷⁷ Thermo-responsive inverse opal films have been fabricated using the colloidal crystal film as a template by backfilling nematic LC monomers, followed by curing and removal of the colloidal template.⁷⁸ They exhibit a spontaneous contraction along the director axis when heated above the nematic-isotropic phase-transition temperature (T_{NI}), resulting from the polymer chains changing to a spherical conformation.⁷⁹ This contraction reduces the diffraction spacing, resulting in a blue shift of the reflectance maximum of the film. The color of cholesteric LCEs can also be changed by tuning the helical pitch of the cholesteric LC phase using mechanical strain.^{80,81}

1.4 Thesis outline

This thesis considers the tuning of optical properties by tailoring and actuating responsive materials. Specifically, we demonstrate the design and fabrication of tilted pillar arrays on wrinkled elastomeric polydimethylsiloxane (PDMS) as a reversibly switchable optical window. Then, we develop a composite film, consisting of a thin layer of quasi-amorphous array of silica nanoparticles (NPs) embedded in bulk elastomeric PDMS, which switches from initial high transparency state to angle-independent coloring upon mechanical stretching. We then consider the micropatterning of nematic liquid crystal elastomer (NLCEs) micropillar arrays that change diameter and height when

heated above the nematic to isotropic phase temperature. The understanding of controlling liquid crystal surface anchoring on micropillars is then applied to self-assemble gold nanorods (AuNRs) into topological defects imposed by the micropillars, leading to dynamic and significant tuning of the surface plasmon resonance properties.

In Chapter 2, we exploit the surface wrinkling effect to reversibly tilt polydimethylsiloxane (PDMS) micropillars. We show that the pattern and wrinkle morphology, orientation and dimensions can be controlled by varying the treatment duration of the oxygen plasma and the angle of uniaxial stretching with respect to the pillar array axis. While the original PDMS film exhibits angle-dependent colorful reflection due to Bragg diffraction of light from the periodic pillar array, the tilted pillar film appears opaque due to random scattering. Upon re-stretching the film to the original pre-strain, the grating color is restored due to the straightened pillars and ~30% transmittance is recovered. Further stretching leads to higher transmittance due to the increasing spacing between the pillars. The switch in optical properties is reversible over many cycles and is applicable for a cheap, controllable optical window.

In Chapter 3, we extend the study of smart windows to incorporate nanoparticles into the PDMS matrix. By embedding refractive-index matching silica nanoparticles, highly transparent (>90% transmittance in the visible wavelength) films are achieved in the initial state. Upon mechanical stretching, the transmittance is dramatically reduced to 30% and displayed angle-independent structural color at a strain >40%. The color could be tuned by the silica NP size. Unlike the silica NPs/PDMS films prepared from highly ordered silica colloidal crystals,⁶⁸ the reflective color is invariant with increased strain.

The switch between transparency and colored states can be reversibly cycled at least 1000 times without losing the film's structural and optical integrity.

In Chapter 4, we develop a new micro-actuator system based on nematic liquid crystal elastomers (NLCEs). Controlling the molecular alignment of nematic liquid crystal (LC) monomers at interfaces before cross-linking plays a key role in manipulating the actuation behavior of NLCE micropillars. Specifically, formation of monodomains of vertically aligned NLC molecules within a pillar array is crucial in maximizing the shape change. A poly(2-hydroxyethyl methacrylate) (PHEMA)-coated PDMS mold is infiltrated with LCs, leading to planar anchoring of LC monomers on the mold surface and vertical alignment within the mold. After cross-linking, the resulting NLCE pillars show a relatively large radial strain (~30%) when heated above nematic to isotropic transition temperature, which can be recovered upon cooling.

In Chapter 5, we extend the understanding of liquid crystal anchoring to achieve the self-assembly of AuNRs for dynamic tuning of the surface plasmonic properties. By exploiting the confinement of the smectic liquid crystal, 4-octyl-4'-cyanobiphenyl (8CB), to topologically patterned pillars, defects can be formed at precise locations around each pillar and tuned by varying the temperature of the system. By dispersing AuNRs in the liquid crystal prior to drop-casting, the nanorods can be directly assembled into the defect structure. Due to the temperature responsiveness of the liquid crystals, the dimensions of the defect structure and consequently, the nanorod assembly can be altered by heating and cooling. As the nanorod assembly changes, the plasmon peaks shift with temperature. By optimizing the surface anchoring conditions and dimensions of the pillar arrays, the plasmon peak shift can be maximized. For epoxy pillars with perpendicular anchoring with aspect ratio 1.3, the transverse and longitudinal local surface plasmon peak shift are

~100 and ~153 nm, respectively. These shifts are reversible over several heating and

cooling cycles.

In Chapter 6, the dissertation is summarized and the outlook and extensions of the current work are discussed.

1.5 References

- 1 Ge, D. *et al.* A robust smart window: Reversibly switching from high transparency to angle-independent structural color display. *Advanced Materials* **27**, 2489, doi:10.1002/adma.201500281 (2015).
- 2 Lee, E. & Yang, S. Bio-inspired responsive polymer pillar arrays. *MRS Communications* **FirstView**, 1, doi:doi:10.1557/mrc.2015.18 (2015).
- 3 Cheng, Y. T., Rodak, D., Wong, C. & Hayden, C. Effects of micro-and nanostructures on the self-cleaning behaviour of lotus leaves. *Nanotechnology* **17**, 1359, doi:10.1088/0957-4484/17/5/032 (2006).
- 4 Barthlott, W. & Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **202**, 1, doi:10.1007/s004250050096 (1997).
- 5 Neinhuis, C. & Barthlott, W. Characterization and distribution of water-repellent, self-cleaning plant surfaces. *Ann Bot-London* **79**, 667, doi:10.1006/anbo.1997.0400 (1997).
- 6 Kinoshita, S., Yoshioka, S. & Kawagoe, K. Mechanisms of structural colour in the morpho butterfly: Cooperation of regularity and irregularity in an iridescent scale. *P Roy Soc B-Biol Sci* **269**, 1417, doi:10.1098/rspb.2002.2019 (2002).
- 7 Potyrailo, R. A. *et al.* Morpho butterfly wing scales demonstrate highly selective vapour response. *Nature Photonics* **1**, 123, doi:10.1038/nphoton.2007.2 (2007).
- 8 Vukusic, P., Sambles, J., Lawrence, C. & Wootton, R. Quantified interference and diffraction in single morpho butterfly scales. *P Roy Soc B-Biol Sci* **266**, 1403, doi:10.1098/rspb.1999.0794 (1999).
- 9 Gao, H., Wang, X., Yao, H., Gorb, S. & Arzt, E. Mechanics of hierarchical adhesion structures of geckos. *Mech Mater* **37**, 275, doi:10.1016/j.mechmat.2004.03.008 (2005).
- 10 Autumn, K. *et al.* Evidence for van der waals adhesion in gecko setae. *Proceedings of the National Academy of Sciences of the United States of America* **99**, 12252, doi:10.1073/pnas.192252799 (2002).
- 11 Autumn, K. & Peattie, A. M. Mechanisms of adhesion in geckos. *Integrative and Comparative Biology* **42**, 1081, doi:10.1093/icb/42.6.1081 (2002).

- 12 Bae, W.-G. *et al.* 25th anniversary article: Scalable multiscale patterned structures inspired by nature: The role of hierarchy. *Advanced Materials* **26**, 675, doi:10.1002/adma.201303412 (2014).
- 13 Hu, Z. B., Chen, Y. Y., Wang, C. J., Zheng, Y. D. & Li, Y. Polymer gels with engineered environmentally responsive surface patterns. *Nature* **393**, 149, doi:10.1038/30205 (1998).
- 14 Liu, M., Wang, S. & Jiang, L. Bioinspired multiscale surfaces with special wettability. *MRS Bulletin* **38**, 375, doi:10.1557/mrs.2013.100 (2013).
- 15 Zhang, J. & Han, Y. Active and responsive polymer surfaces. *Chem Soc Rev* **39**, 676, doi:10.1039/b816231j (2010).
- 16 Christie, R. Colour chemistry. 2 edn, (Royal Society of Chemistry, 2014).
- 17 Kinoshita, S. & Yoshioka, S. Structural colors in nature: The role of regularity and irregularity in the structure. *ChemPhysChem* **6**, 1442, doi:10.1002/cphc.200500007 (2005).
- 18 Kinoshita, S., Yoshioka, S. & Miyazaki, J. Physics of structural colors. *Reports on Progress in Physics* **71**, 076401 (2008).
- 19 Srinivasarao, M. Nano-optics in the biological world: Beetles, butterflies, birds, and moths. *Chem Rev* **99**, 1935, doi:10.1021/cr970080y (1999).
- 20 Joannopoulos, J. D., Johnson, S. G., Winn, J. N. & Meade, R. D. *Photonic* crystals: Molding the flow of light. (Princeton university press, 2011).
- 21 Wiscombe, W. J. Improved mie scattering algorithms. *Appl. Opt.* **19**, 1505, doi:10.1364/AO.19.001505 (1980).
- 22 Zhao, Y., Xie, Z., Gu, H., Zhu, C. & Gu, Z. Bio-inspired variable structural color materials. *Chem Soc Rev* **41**, 3297, doi:10.1039/C2CS15267C (2012).
- 23 Whitney, H. M. *et al.* Floral iridescence, produced by diffractive optics, acts as a cue for animal pollinators. *Science* **323**, 130, doi:10.1126/science.1166256 (2009).
- 24 Liu, F., Dong, B. Q., Liu, X. H., Zheng, Y. M. & Zi, J. Structural color change in longhorn beetles tmesisternus isabellae. *Opt Express* 17, 16183, doi:10.1364/OE.17.016183 (2009).
- 25 Vukusic, P. & Sambles, J. R. Photonic structures in biology. *Nature* **424**, 852, doi:10.1038/nature01941 (2003).
- 26 Takeoka, Y. Angle-independent structural coloured amorphous arrays. *Journal of Materials Chemistry* **22**, 23299, doi:10.1039/C2JM33643J (2012).
- 27 Stavenga, D. G., Leertouwer, H. L., Marshall, N. J. & Osorio, D. Dramatic colour changes in a bird of paradise caused by uniquely structured breast feather barbules. *P Roy Soc B-Biol Sci*, doi:10.1098/rspb.2010.2293 (2010).
- 28 Holt, A. L., Sweeney, A. M., Johnsen, S. & Morse, D. E. A highly distributed bragg stack with unique geometry provides effective camouflage for loliginid squid eyes. *Journal of The Royal Society Interface* 8, 1386, doi:10.1098/rsif.2010.0702 (2011).
- 29 Rassart, M., Colomer, J., Tabarrant, T. & Vigneron, J. Diffractive hygrochromic effect in the cuticle of the hercules beetle dynastes hercules. *New Journal of Physics* **10**, 033014, doi:10.1088/1367-2630/10/3/033014 (2008).

- 30 Vigneron, J. P. *et al.* Switchable reflector in the panamanian tortoise beetle charidotella egregia (chrysomelidae: Cassidinae). *Phys Rev E* **76**, 031907, doi:10.1103/PhysRevE.76.031907 (2007).
- 31 Zylinski, S. & Johnsen, S. Mesopelagic cephalopods switch between transparency and pigmentation to optimize camouflage in the deep. *Curr Biol* **21**, 1937, doi:10.1016/j.cub.2011.10.014 (2011).
- 32 Mäthger, L. M., Denton, E. J., Marshall, N. J. & Hanlon, R. T. Mechanisms and behavioural functions of structural coloration in cephalopods. *Journal of the Royal Society Interface* **6**, S149, doi:10.1098/rsif.2008.0366.focus (2009).
- 33 Izumi, M. *et al.* Changes in reflectin protein phosphorylation are associated with dynamic iridescence in squid. *Journal of The Royal Society Interface* **7**, 549, doi:10.1098/rsif.2009.0299 (2010).
- 34 Ohzono, T., Monobe, H., Shiokawa, K., Fujiwara, M. & Shimizu, Y. Shaping liquid on a micrometre scale using microwrinkles as deformable open channel capillaries. *Soft Matter* **5**, 4658, doi:10.1039/B912235d (2009).
- 35 Haraguchi, K., Li, H. J., Song, L. & Murata, K. Tunable optical and swelling/deswelling properties associated with control of the coil-to-globule transition of poly (n-isopropylacrylamide) in polymer-clay nanocomposite gels. *Macromolecules* **40**, 6973, doi:10.1021/Ma071348i (2007).
- 36 Kim, J., Yoon, J. & Hayward, R. C. Dynamic display of biomolecular patterns through an elastic creasing instability of stimuli-responsive hydrogels. *Nature Materials* **9**, 159, doi:10.1038/Nmat2606 (2010).
- 37 Haraguchi, K. & Takehisa, T. Nanocomposite hydrogels: A unique organicinorganic network structure with extraordinary mechanical, optical, and swelling/de-swelling properties. *Advanced Materials* 14, 1120, doi:10.1002/1521-4095(20020816)14:16<1120::Aid-Adma1120>3.0.Co;2-9 (2002).
- 38 Jeong, K.-U. *et al.* Colour-tunable spiral photonic actuators. *Journal of Materials Chemistry* **19**, 1956, doi:Doi 10.1039/B822980p (2009).
- 39 Lee, C. H., Lim, H. S., Kim, J. & Cho, J. H. Counterion-induced reversibly switchable transparency in smart windows. *ACS Nano* **5**, 7397, doi:10.1021/nn202328y (2011).
- 40 Ahn, S.-k., Kasi, R. M., Kim, S.-C., Sharma, N. & Zhou, Y. Stimuli-responsive polymer gels. *Soft Matter* **4**, 1151, doi:10.1039/B714376a (2008).
- 41 Dai, S., Ravi, P. & Tam, K. C. Ph-responsive polymers: Synthesis, properties and applications. *Soft Matter* **4**, 435, doi:10.1039/B714741d (2008).
- 42 Ge, J. & Yin, Y. Responsive photonic crystals. *Angewandte Chemie International Edition* **50**, 1492, doi:10.1002/anie.200907091 (2011).
- 43 Gupta, P., Vermani, K. & Garg, S. Hydrogels: From controlled release to phresponsive drug delivery. *Drug Discovery Today* **7**, 569, doi:10.1016/S1359-6446(02)02255-9 (2002).
- 44 Liu, F. & Urban, M. W. Recent advances and challenges in designing stimuliresponsive polymers. *Prog Polym Sci* **35**, 3, doi:10.1016/j.progpolymsci.2009.10.002 (2010).

- 45 Roy, D., Cambre, J. N. & Sumerlin, B. S. Future perspectives and recent advances in stimuli-responsive materials. *Prog Polym Sci* **35**, 278, doi:10.1016/j.progpolymsci.2009.10.008 (2010).
- 46 Stuart, M. A. *et al.* Emerging applications of stimuli-responsive polymer materials. *Nature Materials* **9**, 101, doi:10.1038/nmat2614 (2010).
- 47 Zhao, Y. & Ikeda, T. Smart light-responsive materials: Azobenzene-containing polymers and liquid crystals. (John Wiley & Sons, 2009).
- 48 Dong, L., Agarwal, A. K., Beebe, D. J. & Jiang, H. Adaptive liquid microlenses activated by stimuli-responsive hydrogels. *Nature* **442**, 551, doi:10.1038/nature05024 (2006).
- 49 Schmaljohann, D. Thermo-and ph-responsive polymers in drug delivery. *Adv Drug Deliver Rev* **58**, 1655, doi:10.1016/j.addr.2006.09.020 (2006).
- 50 Weissman, J. M., Sunkara, H. B., Albert, S. T. & Asher, S. A. Thermally switchable periodicities and diffraction from mesoscopically ordered materials. *Science* **274**, 959, doi:10.1126/science.274.5289.959 (1996).
- 51 Takeoka, Y. & Watanabe, M. Template synthesis and optical properties of chameleonic poly(n-isopropylacrylamide) gels using closest-packed self-assembled colloidal silica crystals. *Advanced Materials* **15**, 199, doi:10.1002/adma.200390044 (2003).
- 52 Takeoka, Y. & Watanabe, M. Tuning structural color changes of porous thermosensitive gels through quantitative adjustment of the cross-linker in pre-gel solutions. *Langmuir* **19**, 9104, doi:10.1021/la035142w (2003).
- 53 Honda, M., Seki, T. & Takeoka, Y. Dual tuning of the photonic band-gap structure in soft photonic crystals. *Advanced Materials* **21**, 1801, doi:10.1002/adma.200801258 (2009).
- 54 Lee, K. & Asher, S. A. Photonic crystal chemical sensors: Ph and ionic strength. *Journal of the American Chemical Society* **122**, 9534, doi:10.1021/ja002017n (2000).
- 55 Holtz, J. H. & Asher, S. A. Polymerized colloidal crystal hydrogel films as intelligent chemical sensing materials. *Nature* **389**, 829 (1997).
- 56 Honda, M., Kataoka, K., Seki, T. & Takeoka, Y. Confined stimuli-responsive polymer gel in inverse opal polymer membrane for colorimetric glucose sensor. *Langmuir* **25**, 8349, doi:10.1021/la804262b (2009).
- 57 Wang, Z. *et al.* Organic-inorganic hybrid photonic hydrogels as a colorful platform for visual detection of scn. *Chem Commun* **46**, 8636, doi:10.1039/C0CC03533E (2010).
- 58 Kamenjicki, M., Lednev, I. K., Mikhonin, A., Kesavamoorthy, R. & Asher, S. A. Photochemically controlled photonic crystals. *Advanced Functional Materials* **13**, 774, doi:10.1002/adfm.200304424 (2003).
- 59 Kamenjicki Maurer, M., Lednev, I. K. & Asher, S. A. Photoswitchable spirobenzopyran- based photochemically controlled photonic crystals. *Advanced Functional Materials* **15**, 1401, doi:10.1002/adfm.200400070 (2005).
- 60 Matsubara, K., Watanabe, M. & Takeoka, Y. A thermally adjustable multicolor photochromic hydrogel. *Angewandte Chemie International Edition* **46**, 1688, doi:10.1002/anie.200603554 (2007).

- 61 Kloxin, C. J. & Bowman, C. N. Covalent adaptable networks: Smart, reconfigurable and responsive network systems. *Chem Soc Rev* **42**, 7161, doi:10.1039/c3cs60046g (2013).
- 62 Lendlein, A. & Kelch, S. Shape-memory polymers. *Angewandte Chemie International Edition* **41**, 2034, doi:10.1002/1521-3773(20020617)41:12<2034::AID-ANIE2034>3.0.CO;2-M (2002).
- 63 Liu, C., Qin, H. & Mather, P. Review of progress in shape-memory polymers. *Journal of Materials Chemistry* **17**, 1543, doi:Doi 10.1039/B615954k (2007).
- 64 Li, J. *et al.* Switching periodic membranes via pattern transformation and shape memory effect. *Soft Matter* **8**, 10322, doi:10.1039/C2sm25816a (2012).
- 65 Xu, H. *et al.* Deformable, programmable, and shape-memorizing micro-optics. *Advanced Functional Materials* **23**, 3299, doi:10.1002/adfm.201203396 (2013).
- 66 Lötters, J., Olthuis, W., Veltink, P. & Bergveld, P. The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications. *Journal* of Micromechanics and Microengineering 7, 145, doi:10.1088/0960-1317/7/3/017 (1997).
- 67 Xia, Y. & Whitesides, G. M. Soft lithography. *Annual Review of Materials Science* **28**, 153, doi:10.1146/annurev.matsci.28.1.153 (1998).
- 68 Fudouzi, H. & Sawada, T. Photonic rubber sheets with tunable color by elastic deformation. *Langmuir* **22**, 1365, doi:10.1021/la0521037 (2005).
- 69 Warner, M. & Terentjev, E. M. *Liquid crystal elastomers*. Vol. 120 (Oxford University Press, 2003).
- 70 Li, M.-H. & Keller, P. Artificial muscles based on liquid crystal elastomers. *Phil Trans R Soc A* **364**, 2763, doi:10.1098/rsta.2006.1853 (2006).
- 71 Spillmann, C. M., Naciri, J., Chen, M.-S., Srinivasan, A. & Ratna, B. R. Tuning the physical properties of a nematic liquid crystal elastomer actuator. *Liq Cryst* 33, 373 doi:10.1080/02678290500494921 (2006).
- 72 Thomsen, D. L. *et al.* Liquid crystal elastomers with mechanical properties of a muscle. *Macromolecules* **34**, 5868, doi:10.1021/Ma001639q (2001).
- 73 Xie, P. & Zhang, R. Liquid crystal elastomers, networks and gels: Advanced smart materials. *Journal of Materials Chemistry* **15**, 2529, doi:10.1039/B413835J (2005).
- 74 Alexander, G. P., Chen, B. G.-g., Matsumoto, E. A. & Kamien, R. D. Colloquium: Disclination loops, point defects, and all that in nematic liquid crystals. *Reviews of Modern Physics* 84, 497, doi:10.1103/RevModPhys.84.497 (2012).
- 75 Kim, Y. H., Yoon, D. K., Jeong, H. S., Lavrentovich, O. D. & Jung, H.-T. Smectic liquid crystal defects for self-assembling of building blocks and their lithographic applications. *Advanced Functional Materials* 21, 610, doi:10.1002/adfm.201001303 (2011).
- 76 Spillmann, C. M., Ratna, B. R. & Naciri, J. Anisotropic actuation in electroclinic liquid crystal elastomers. *Applied Physics Letters* **90**, 021911, doi:10.1063/1.2420780 (2007).

- 77 Rousseau, I. A. & Mather, P. T. Shape memory effect exhibited by smectic-c liquid crystalline elastomers. *Journal Of the American Chemical Society* **125**, 15300, doi:10.1021/ja039001s (2003).
- 78 Wu, G. *et al.* Thermoresponsive inverse opal films fabricated with liquid-crystal elastomers and nematic liquid crystals. *Langmuir* **27**, 1505, doi:10.1021/la1037124 (2011).
- 79 Jin, L. H., Lin, Y. & Huo, Y. Z. A large deflection light-induced bending model for liquid crystal elastomers under uniform or non-uniform illumination. *Int J Solids Struct* 48, 3232, doi:10.1016/j.ijsolstr.2011.07.015 (2011).
- 80 Castles, F. *et al.* Stretchable liquid-crystal blue-phase gels. *Nat Mater* **13**, 817, doi:10.1038/nmat3993 (2014).
- 81 Schmidtke, J., Kniesel, S. & Finkelmann, H. Probing the photonic properties of a cholesteric elastomer under biaxial stress. *Macromolecules* **38**, 1357, doi:10.1021/ma0487655 (2005).

CHAPTER 2: Tilted pillars on wrinkled elastomers as a reversibly

tunable optical window

Adapted from:

Lee, E., Zhang, M., Cho, Y., Cui, Y., Van der Spiegel, J., Engheta, N. and Yang, S. (2014), Tilted Pillars on Wrinkled Elastomers as a Reversibly Tunable Optical Window. Adv. Mater., 26: 4127–4133.¹ Reproduced with permission.

2.1 Introduction

Switchable optical materials, which possess reversible light transmission properties in response to external stimuli, are of wide interest for potential applications such as windows and skylights in architectural and vehicular settings that can block or transmit light. Switchable optical properties have been achieved using suspended particles,² polymer dispersed liquid crystals,³⁻⁷ photonic crystals,⁸ and chromogenic materials, driven by light,⁹ temperature¹⁰ and electrical field.¹¹ However, the preparation and fabrication of such smart windows often require expensive equipment, complicated processes, and multi-layered design. In addition, many of these materials are chemically unstable, costly, or difficult to prepare. Thus, process simplification will be highly desired for the fabrication of large-area smart windows.¹² Surfaces patterned with nanoor microscale features offer a new type of smart materials that can change physical properties by dynamically tuning surface geometry in response to external stimuli without altering the bulk properties. They have been utilized for a wide range of applications, including controlled wetting,¹³ adhesion,¹⁴ optical elements,¹⁵ and microfluidics.¹⁶

Previously, many groups have demonstrated the tuning of photonic structures, which are characterized by periodically modulated refractive index, to switch between diffraction colors in response to various stimuli.^{8,17-19} By deforming microstructured periodic membranes that can open and close their pores, our group has demonstrated reversible tuning between diffraction grating color to a transparent window.^{20,21} Further, capillary-force-induced clustering of polymeric micropillar arrays (diameter, 0.75-1 µm, aspect ratio up to 12, pitch, 1.5-2 µm) was exploited for switching from a colored film to ultrathin whiteness to transparency.²² The unique optical properties are realized by a capillary-force-induced instability when drying poly(2-hydoxylmethacrylate-co-methyl methacrylate) (PHEMA-co-PMMA) micropillar arrays of different elastic modulus. The structural color arises from the Bragg diffraction from the straight, highly ordered pillars; the whiteness comes from the laterally collapsed, randomly arranged pillars; and the transparency from the ground collapsed pillars. However, the color of the original pattern is irrecoverable due to large van der Waals force between collapsed pillars. Thus, we envision that when pillars are tilted on a substrate, but not touching each other, it is possible to achieve the dramatic and reversible visual effect between colorful, white, and transparent states by reversibly stretching the pillars from tilted to straight position using mechanical force.

The ability to reversibly change the surface topography on an elastomeric substrate under an external force offers a simple, low-cost, and repeatable method to switch material's optical properties. Compared to methods that use solvent (swelling or drying), pH, electrical field and light, application of mechanical force is simple and will allow for independent control of the amount, direction (uniaxial vs. biaxial, in-plane vs.

out-of-plane), and timing of strain to tune the surface features. In nature, chameleon and bobtail squids stretch out their skins to enlarge the chromophores embedded in the skins, thereby switching the body color for signaling or escape from predators.²³ As mentioned earlier, we observed switching from grating color to ultrathin whiteness to transparency when collapsing the high-aspect-ratio (sub)micron pillar array (diameter of 750 nm and 1 μ m, height of 9 μ m).²² However, the color change is not reversible due to the permanent collapse of the pillars. It will be ideal if we can tilt the pillars such that they can intersect without touching each other, and the pillars can be reversibly changed from tilted, an analog of collapsed state, to a vertically aligned, highly ordered state.

Previously researchers have created tilted polymeric pillars using techniques, including oblique metal deposition,²⁴ ion beam irradiation,²⁵ and shearing of shape memory polymers.^{26,27} The resulting pillars can achieve one-directional tilting but the tilting is often non-reversible. We and others have shown that microwrinkles can be reversibly stretched and released to change surface topography for tunable wetting and adhesion.^{13,14,28} This begs the question of whether wrinkling can be exploited to manipulate the dimensions and orientation of a micropillar array, i.e. reversible tilting. Lee *et al.* have reported the reversible wrinkling of nanopillar arrays on a microwrinkled surface for mechanically tunable wetting and transparency.²⁸ In their system, nanopillars are slightly tilted near the valleys of the microwrinkles and the contribution of pillar tilting to the optical property should be minimal due to the large mismatch of the pillar (diameter = 150 nm) and wrinkle dimensions (periodicity $\lambda = 31 \ \mu m$ and amplitude A=4.4 \ \mum). Therefore, the orientation of the nanopillars are largely unaffected by the wrinkling. The switchable transmission (transparent \leftrightarrow opaque) is achieved primarily by reversibly flattening the light-scattering microwrinkles and no additional structural color change is reported due to the small size of the nanopillars. Kang *et al.*, on the other hand, show that when the spacing ratio (space/diameter) of PDMS micropillars (diameter = 5 μ m and height = 10 μ m)is increased to 6, the film has transmittance greater than 80% in the visible and near IR regions.²⁹ Again, the film is not colored, nor is it tunable. Xu *et al.* and Xie *et al.* have demonstrated the mechanical deformation of microscopically patterned shape memory polymer substrates for tunable optical properties.^{30,31}

These studies intrigued the question of whether it is possible to switch a smart window between three states: opaque, colored and transparent ones by reversibly stretching (sub) micron-sized PDMS pillars atop microwrinkles using mechanical force. Here, we demonstrate the design and fabrication of tilted pillar arrays on wrinkled elastomeric polydimethylsiloxane (PDMS) as a reversibly switchable optical window. We exploit the surface wrinkling effect to reversibly tilt polydimethylsiloxane (PDMS) micro-pillars. Using square arrays of microposts (diameter 1µm, pitch 2µm, and height 4µm), the wrinkle formation can be confined to the micropattern. We show that the pattern and wrinkle morphology, orientation and dimensions were controlled by varying the treatment duration of the oxygen plasma and the angle of uniaxial stretching with respect to the pillar array axis. While the original PDMS film exhibited angle-dependent colorful reflection due to Bragg diffraction of light from the periodic pillar array, the tilted pillar film appeared opaque. Upon re-stretching the film to the original pre-strain, the grating color is restored due to the straightened pillars and $\sim 30\%$ transmittance is recovered. Further stretching led to higher transmittance due to the increasing spacing

between the pillars. The switch in optical properties is completely reversible over many cycles and is applicable for a cheap, controllable optical window.

2.2 Experimental methods

2.2.1 Transmission simulation

Finite-difference time-domain (FDTD) numerical simulation was performed first on a model of a periodic array consisting of micron-sized pillars. A linearly polarized plane wave with a wavelength in the range of 380nm to 680nm was illuminated onto the array vertically from a far field (larger than 5λ) as the incident light. In this simulation, a power monitor was located right under the surface of the substrate to detect the total amount of power passing through the pillar array. The thickness of the substrate, which was in the range of several millimeters, was assumed to be infinite while comparing to the height of the micron-sized pillars, while the pillar array dimensions were varied.

2.2.2 Materials

Dow Corning Sylgard 184 silicone elastomer kit was used for preparing PDMS. Tridecafluorotetrahydrooctyltrichlorosilane (SIT8174.0 from Gelest) was used to render the PDMS surface superhydrophobic

2.2.3 Fabrication of PDMS pillar array

The PDMS pillar array was replica molded from the epoxy pillar arrays master via PDMS membrane, following the procedure reported earlier.³² Briefly, PDMS precursor was mixed with a curing agent in a 10:1 weight ratio, degassed in a vacuum chamber for 1 h. The mixture was poured over the epoxy pillar master (1 μ m diameter, 2 μ m pitch, 4 μ m

height) and cured at 65°C for 4 h. The resulting PDMS membrane was treated with UVO model 144AX) for 1 h. followed deposition (Jelight, by vapor of tridecafluorotetrahydrooctyltrichlorosilane as a release agent overnight to render the surface superhydrophobic. Another degassed mixture of PDMS precursor with 10 wt% curing agent was poured over the treated PDMS membranes and cured at 100°C overnight. After cooled to room temperature, the PDMS pillar array was peeled from the membrane mold.

2.2.4 Surface wrinkling of PDMS substrates

The fabrication followed the procedure reported in literature.³³ Briefly, the molded PDMS film (flat, with the hole array or pillar array) was clamped and stretched uniaxially (ε up to 30%) using a custom-made stretching device. The surface was then treated with oxygen plasma (Technics, model PE11-A) at a power of 100 watts, pressure of 0.5 torr for1-20 min. Wrinkle patterns formed spontaneously upon release of the strain.

2.2.5 Sample characterization

Scanning electron microscopy (SEM) images were taken by FEI Quanta Field Emission Gun Environmental SEM in high vacuum mode at an acceleration voltage of 5kV. The topography of the substrates were examined using a DI Dimension 3000 atomic force microscope (AFM) and images were rendered using WSXM.³⁴ Transmission spectra were taken using a custom-built free-space microscope with a white light source and normalized to a flat PDMS film.

2.2.6 Finite-element analysis

ABAQUS/Standard,³⁵ a commercial finite-element analysis software, was used. Young's modulus and Poisson's ratio of PDMS were chosen to be 2.6 MPa¹⁴ and 0.48.³⁶ We assumed that the oxidized PDMS surface has the same properties as glass, of which Young's modulus and Poisson's ratio were 700 GPa and 0.33, respectively.³⁶ While the thickness of the oxidized layer is generally unknown, here we estimated the thickness of 500 nm for the prediction of buckled shape. Three-dimensional continuum element (C3D6) was adopted with approximately 200 nm in characteristic element length.

2.3 Optical simulation

To demonstrate the feasibility of this approach, we first performed finitedifference time-domain (FDTD) numerical simulation on a model consisting of micronsized pillars in a square array (**Figure 2.1**). A linearly polarized plane wave with a wavelength in the range of 380nm to 680nm was illuminated onto the array vertically from a far field (larger than 5 times the wavelength). The thickness of the substrate, typically in the range of several millimeters, was assumed to be infinite compared to the height of the micron-sized pillars. In the simulation, a power monitor is located right under the surface of the substrate to detect the total amount of optical power passing through the pillar array. The employed model of the first study consisted of pillars with diameter $D = 1 \mu m$, height $H = 4 \mu m$, and the pitch *P* was varied from 1.1 μm to 2 μm . The 1 μm pillar size was chosen here to have grating color in the visible and near IR wavelength.²² In the second study, *P* was fixed at 2 μm , while the aspect ratio (=*H/D*) was varied from 2 to 8 (**Figure 2.1d-f**). Numerical results showed clear variation of the transmittance of the incident wave. Increasing the aspect ratio of the pillars had a relatively minor effect (~20% drop) on the transmission (**Figure 2.1c**) over the simulated wavelengths, whereas increasing the pillar pitch induced an abrupt increase in transmission up to 60% (**Figure 2.1d**). Meanwhile, tilting the pillars (**Figure 2.1e**) induced a gradual drop in transmission with increasing tilt angle (**Figure 2.1g**). These results suggested that a hierarchical structure consisting of tilted pillars atop wrinkles of matching dimensions (**Figure 2.1f**) could lead to a gradual but significant decrease in transmission in the visible wavelength (**Figure 2.1h**), making it possible to design a smart optical window.



Figure 2.1 Simulated optical properties of straight and tilted periodic square pillar array of different dimensions, spacing, aspect ratio and tilt angles. (a-b) Schematic illustration of the straight pillars. (c-d) Transmission spectra of a straight pillar array with (c) varying pitch and (d) aspect ratio. (e-f) Schematic of a single tilted pillar (e) and an array of tilted pillars atop a wrinkled structure (f). (g-h) Transmission spectra of a tilted pillar array with (c) varying tilt angle θ and (d) $\theta = 20^{\circ}$ with varying pitch. All samples are fixed at D = 1 μ m, H = 4 μ m, P = 2 μ m, $\theta = 0^{\circ}$ unless otherwise indicated.

2.4 Wrinkling control

Wrinkles can be generated by thermal stress,³⁷ mechanical stress,^{13,14,33} capillary force,³⁸ and osmotic pressure.³⁹ One simple approach is to treat a pre-strained PDMS substrate by oxygen plasma or UV-ozonlysis (UVO).^{33,36} A hard silica-like skin layer will form on top of the elastomeric PDMS and the mismatch in elastic moduli will cause the substrate to wrinkle when the pre-strain is removed. The wrinkle periodicity in such an elastic bilayer system is given by^{36,40}

$$\lambda = 2\pi t_h \left(\frac{\overline{E_h}}{3\overline{E_s}}\right)^{\frac{1}{3}}$$
(2-1)

where t_h is the film thickness, $\overline{E} = E/(1 - v^2)$ is the plane-strain modulus, E is the Young's modulus, v is the Poisson's ratio, and the subscripts 'h' and 's' refer to the hard thin top layer and the soft bottom substrate, respectively.⁴¹ The amplitude of the wrinkle can be expressed as

$$A = t_h \left(\frac{\varepsilon_0}{\varepsilon_c} - 1\right)^{\frac{1}{2}}$$
(2-2)

where ε_0 is the applied strain and ε_c is the critical strain given by

$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\overline{E_s}}{\overline{E_h}} \right)^{\frac{2}{3}}$$
(2-3)

The thickness and modulus of the silicate layer, and therefore the wrinkle dimensions, depend on the oxygen plasma or UVO treatment power and exposure time. Since PDMS is elastomeric and both layers of the system are derived from the same material, large strain levels can be achieved without delamination and the wrinkles can be reversibly flattened. If pillars are patterned atop the wrinkles, they can be tilted using wrinkling and reversibly straightened. Further stretching of the straightened pillars could change their spacing ratio. The anisotropic and macroscopically-ordered nature of mechanical wrinkles can be used to manipulate pre-patterned substrates to form hierarchically tilted pillars.

In order to exploit the interplay between the optical properties of periodically ordered micropillar arrays and reversibly tunable wrinkles, we fabricated PDMS pillars in a square array atop mechanically-induced wrinkles, with the wrinkle periodicity concurrent to the pitch of the pillar array. Here, we chose a micropillar array (diameter = $1 \mu m$, pitch = $2 \mu m$, height = $4 \mu m$) due to its inherent colorful appearance, resulting from Bragg diffraction of light. To match the pitch of the array, oxygen plasma was chosen to induce wrinkling since the typical periodicity of oxygen plasma treated wrinkles ranges from 300 nm to 10 μm .⁴¹ The PDMS pillar film was stretched uniaxially to 30% strain, followed by oxygen plasma treatment. Upon releasing the pre-strain, microwrinkles were formed as a result of balancing the compressive strain and elastic bending strain energy (**Figure 2.2a**).



Figure 2.2 (a) Schematic of a square PDMS pillar array, stretched, treated with oxygen plasma, and released to form wrinkles with low amplitude. (b) For the flat bilayer system, the thickness is a constant regardless of in-plane direction. (c) The thickness is a function of in-plane position in the case of bilayer system with pillar array.

The introduction of a pre-pattern, here, a pillar array, altered the stress relief upon releasing the strain. According to Equation (2-1), the wrinkle periodicity is directly proportional to the thickness of the modified thin film. If the elastic bilayer system is flat, i.e. t_h is a constant along all directions (**Figure 2.2b**), wrinkle generation is expected to be independent from the stretching direction, defined in **Figure 2.2a** as *y*. In the prepatterned system, however, t_h is a function of position and discontinuous (**Figure 2.2c**). Rotation of the stretching direction is equivalent to varying the thickness function, leading to distinct wrinkle morphologies in relation to the pillar array. In this case, wrinkle formation cannot be described by Equation (2-2), which applies to a flat bilayer system as shown in (**Figure 2.2b**). In the micropillar pre-patterned system, each pillar shields the bottom substrate from oxygen plasma treatment, thereby reducing the effective thickness (**Figure 2.2c**). Therefore the film thickness, t_h , becomes a function of position. While this thickness function has obvious discontinuity at the pillar boundary, we can describe a generalized form of wrinkle periodicity without losing continuity by adding the weighing factor of wavelength, Ω_{λ} , which is given by

$$\lambda = \Omega_{\lambda}(x) 2\pi t_h(x) \left(\frac{\overline{E_h}}{3\overline{E_s}}\right)^{\frac{1}{3}}$$
(2-4)

where *x* is the in-plane position vector. The generalized form of the amplitude of wrinkle is expressed as

$$A = \Omega_{\rm A}(x)t_h(x)\left(\frac{\varepsilon_0}{\varepsilon_c} - 1\right)^{\frac{1}{2}}$$
(2-5)

where Ω_A is the weighing factor of amplitude. When we take a constant thickness for $t_h(x)$ and 1.0 for each weighing factor, we obtain the expression for flat bilayer system, Equation (2-1) and (2-2) again. Depending on the pillar dimension and its arrangement, the thickness function can be expressed as

$$t_h \begin{cases} t_f \ (x \not\subset S_p) \\ 0 \ (x \subseteq S_p) \end{cases}$$
(2-6)

where t_f is the film thickness without consideration of pillar height and S_p is the in-plane space (\mathbf{R}^2) in which the pillars are located.

This is different from confined wrinkling typically reported in literature, where wrinkles are confined to a pre-pattern of much larger size such that surface wrinkling size is not affected by the pre-pattern.^{36,42} Our prior study shows that when the pre-pattern size is comparable to the wrinkle periodicity, the wrinkles lose their isotropic nature completely and their formation is dominated by the edge effect of the pre-patterns.⁴³ Therefore, they are aligned perpendicularly to the pre-pattern wave vector.

Here, when the PDMS pillar film was pre-strained along the pattern and treated with oxygen plasma for 1 min, wrinkles formed along the pattern, in the direction x, with periodicity similar to the pillar pitch ($\sim 2 \mu m$), and the pillars were found atop the wrinkles (Figure 2.3b-c). However, in the region without pillars, wrinkles were shown to have a much smaller periodicity (~0.7µm) as measured by AFM (Figure 2.3a). This resulted in a transition region at the edge of the pillar pattern, in which the wrinkle periodicity changes to match the pillar pitch (Figure 2.3d). When stretched at an angle θ = 45° to the pillar axis (defined as k axis), wrinkles with periodicity similar to pillar pitch were observed with appearance of secondary wrinkles forming an "X" between the pillars (Figure 2.3e). A tilted SEM image shows that the pillars are still vertical (Figure 2.3f) and there is a transition region at the pattern edge (Figure 2.3g). When stretched at θ $=30^{\circ}$ and 60° , respectively, the wrinkles undulated to accommodate the pillars (Figure **2.3**h-m), leading to change of wrinkle periodicity depending on the position of the pillars and an interesting transition of the wrinkle dimensions from the flat region to the patterned region (Figure 2.3j, m).



Figure 2.3 (a) AFM image and height profile of wrinkles formed using oxygen plasma for 1 minute. SEM images of wrinkled PDMS with pillar arrays fabricated by stretching the PDMS film at an angle of (b-d) 0° , (e-g) 45° , (h-j) 30° , and (k-m) 60° to the k axis of

the 2D pattern, followed by oxygen plasma for 1 min, and release of the strain. SEM images of the samples tilted at 30° (c, f, i, l) and the transition region of wrinkles to pillars at the edge of the pattern (d, g, j, m). Scale bar: 2 μ m.

While slight changes to the film transparency were observed in these films, the low wrinkle amplitude (~250 nm) limited such effects. The amplitude of the wrinkles is proportional to the thickness of the top thin hard layer, as given by Equation (2-2). Thus, PDMS film treated by oxygen plasma for a longer time should generate wrinkles with higher amplitudes. To support our hypothesis, finite element simulation (Figure 2.4) was performed to better understand the effect of a thicker silicate layer on the wrinkle morphology of PDMS substrates with micropillar arrays. The buckling behaviors of pillar array on PDMS substrate were simulated based on the concept of a representative unit structure. The dimension of a unit structure was determined as the lattice structure with respect to the stretching direction (Figure 2.4a). The periodic boundary condition (PBC)⁴⁴ was imposed on the cross-sectional face in all sides of the unit structure, as shown in Figure 2.4b, to maintain the periodicity in the course of buckling. Stress-free condition was assumed for the oxidized layer before the strain release, because the layer was formed after stretching (pre-strain $\varepsilon \sim 30\%$). The thickness of the oxidized layer due to oxygen plasma is generally unknown, and can be in a range of $10-1000 \text{ nm}^{36}$. Here, we assumed a thickness of 500 nm for the oxidized layer. The predicted buckling modes after strain release are shown in Figure 2.4c.



Figure 2.4 Finite element simulation. (a) Unit structures (marked in red) with respect to the reference stretching direction. $\arctan(0)=0^{\circ}$, $\arctan(1/2)\sim30^{\circ}$, and $\arctan(1)=45^{\circ}$, respectively. (b) Pre-stretched state. Yellow dotted lines indicate the reference lattice direction. Arrows indicate the stretching directions. (c) Predicted buckling modes. Top thin film with pillar array shows anisotropic buckling mode with respect to the stretching direction.

As expected, wrinkles with higher amplitude were obtained in simulation, thus, tilting the pillar arrays. Experimentally, for an oxygen plasma treatment time of 20 min, both larger amplitude (~700 nm) and periodicity (~2.4 μ m) were observed (**Figure 2.5a**) for flat PDMS films. These wrinkles assumed the sinusoidal morphology of wrinkles formed from non-patterned films. Thus, the wrinkles formed under the micropillars tilted the pillars at variable degrees depending on the original pre-strain angle.

For films stretched parallel to the pattern direction, *k* axis, pillars on the same wrinkle tilt in the same direction along the wrinkle but in opposite directions of those on the neighboring wrinkles (**Figure 2.5f**). At $\theta = 45^{\circ}$, the pillars tilted in alternating directions (perpendicular to the wrinkle) with each other along the long axis of the wrinkles, forming a mesh-like structure (**Figure 2.5g**). It is important to note here that the pillars did not touch each other. Similar alternating tilting was observed in substrates prestretched at 30° and 60°, respectively (**Figure 2.5h-i**). However, the tilting of the pillars was not perpendicular to the wrinkle. Therefore, the tilted pillars could touch each other. SEM images of the transition region between the patterned and non-patterned areas showed that the wrinkles no longer undulated to accommodate the pillars; rather the pillars tilted atop the larger wrinkles (**Figure 2.5j-m**). The experimental results matched well with the simulation, with the tilting of the pillars depending on the angle between the stretching direction *y* and the pillar direction *k* (**Figure 2.5b-e**).



Figure 2.5 (a) AFM image and height profile of wrinkles formed using oxygen plasma for 20 minutes. Finite-element simulation and corresponding SEM images of PDMS wrinkles with pillar arrays stretched at an angle of (b, f) 0° , (c, g) 45° , (d, h) 30° , and (e, i) 60° to the pattern and treated with oxygen plasma for 20 minutes. SEM images of the transition region of wrinkles to pillars at the edge of the pattern (j-m). Scale bar: 2 µm. (n) Schematic of a square pillar array overlaying wrinkles.

The angle of the pillar tilting can be estimated using geometric analysis (**Figure 2.5n**), where the wrinkle direction is defined as the *x*-axis. The wrinkle can be fitted with a sinusoidal curve:

$$z = \frac{A}{2} - \frac{A}{2} \cos\left(\frac{2\pi x}{\lambda}\right) \tag{2-7}$$

Here, the valley of the wrinkle is located at x = 0 and the peak position is located at $x = \lambda/2$. The slope at a given position along the wrinkle can then be expressed as:

$$\frac{\partial z}{\partial x} = \frac{\pi A}{\lambda} \sin\left(\frac{2\pi x}{\lambda}\right) \tag{2-8}$$

A pillar is spaced p from its nearest pillar and its distance along the *x*-axis can be calculated as $p\cos\theta$. By aligning the peak of the wrinkle with the halfway point between the pillars, the distance of the pillar x = a from the valley from the wrinkle is therefore $(\lambda - p\cos\theta)/2$. The tilting angle of the bottom edge of the pillar (ϕ) with the horizontal at position x = a can then be calculated as:

$$\phi = \tan^{-1} \left(\frac{\partial z}{\partial x} \right)_{x=a} \tag{2-9}$$

The nearest pillar is located at position $b = pcos\theta + (\lambda - pcos\theta)/2$. The next nearest pillar is located at an angle of θ +45° from the *x*-axis and its position *c* can be calculated as

$$c = p\sqrt{2}\cos(\theta + 45^{\circ}) + \frac{\lambda - p\cos\theta}{2}$$
(2-10)

By plugging in the dimensions of the pillar array and wrinkle, the tilting angle of the pillars can be calculated for samples pre-stretched at various angles (see summary in **Table 2.1**). It is notable that for samples pre-stretched at 45°, all tilting angles of the pillars ϕ at different positions are equivalent to each other but in opposite directions, whereas those from pre-stretching angles at 30° and 60° depend on the pillar position relative to the pillar at which the origin is defined. This is confirmed by SEM (Figure 3b-d).

Table 2.1 Tilting angle of the pillars, ϕ , calculated geometrically. The pillar dimensions, diameter $d = 1 \ \mu m$ and pitch $p = 2 \ \mu m$. The wrinkle had periodicity $\lambda = 2.4 \ \mu m$, and amplitude A = 750 nm.

θ [°]	<i>a</i> [µm]	<i>b</i> [µm]	<i>c</i> [µm]	ϕ at a [°]	ϕ at b [°]	ϕ at c [°]
30	0.33	2.07	1.07	20.63	-20.63	9.57
45	0.49	1.91	0.49	25.25	-25.25	25.25
60	0.70	1.70	-0.30	25.37	-25.37	-2.36

2.5 **Optical response**

The observed tilting disrupted the ordering of the originally square array pillars, causing a sharp decrease in the optical transmittance due to scattering on the pillar surface and the wrinkle surface. Unlike the previous observation of irreversible whitening from the clustered pillar arrays, the optical transmittance can be recovered upon stretching the PDMS films since the pillars did not bundle together but tilted in-between.

The switchability of transmission was characterized by UV-vis spectrophotometry using a custom-built free-space microscope. The film optical transmittance was measured as a function of wavelength at various strain levels (Figure 2.6a). The as-prepared substrate, stretched at 60° to the pattern, was optically opaque with an average transmission of 42.1±0.4% at wavelengths 500-700 nm (Figure 2.6d). When stretching the film to the maximum pre-strain (\sim 30%), the average transmission increased to 71.1±2.1% over the same wavelength range (Figure 2.6c). Accordingly, the grating color of the periodic pillar array was recovered and can be observed with incident light at an angle to the substrate (Figure 2.6f). Upon further stretching to 40% strain (i.e. beyond the original pre-strain to increase the pillar spacing), the transmission increased to $77.4\pm0.1\%$. Stretching of the substrates within an SEM showed that the tilted pillars of the asprepared substrate reverted to their vertical positions while the wrinkles were nearly flattened upon stretching to the original 30% pre-strain (Figure 2.6h-k). Upon release of the strain, the pillars again became tilted and the film whitened. Such transition from opaqueness to a colored film can be repeated mechanically and reversibly by stretching and releasing the underlying wrinkles.



Figure 2.6 (a) Transmission spectrum of a wrinkled PDMS film (pre-stretched at an angle of 60°) with a pillar array at various strains. Digital photograph of the substrate with incident light normal to the sample at (b) 40%, (c) 30% and (d) 0% strain. (e-g) Corresponding photographs of the substrate with incident light fixed at an angle to the sample. SEM images of wrinkled PDMS re-stretched to a strain of (h) 0%, (i) 10%, (j) 20%, and (k) 30% (Scale bars 4 μ m).

To demonstrate mechanical robustness, the substrate was stretched and released for over 50 cycles. The transmission of the sample was measured again at 0% and 30% strain to be $42.7\pm1.7\%$ and $63.3\pm0.8\%$, respectively (**Figure 2.7**). The latter decreased somewhat after 50 cycles, possibly due to formation of cracks and other defects in the film. We believe depositing a more compliant material (e.g. metal) on an elastomeric substrate (e.g. shape memory polymer above its glass transition temperature) could minimize the crack formation in oxidized PDMS films. Our initial study supported this. Nevertheless, the transition between color and opaqueness is reversible and repeatable over many cycles without any mechanical failure.



Figure 2.7 Transmission spectrum of a wrinkled PDMS film with a pillar array at 0% and 30% strain measured at different stretch/release cycles. The number of cycles was indicated in the bracket.

For comparison, we also characterized the regions without pillars, which had an intrinsic periodicity of ~2 μ m (treated with oxygen plasma for 20 min). The wrinkled film appeared opaque with an average measured transmission of 55.1±1.1% from 500-700 nm relative to a flat PDMS film of comparable thickness (**Figure 2.8a, c**). When restretching the film to 30% strain, this region becomes highly transparent (Figure S3b) with an average transmission of 87.1±1.1% over 500-700 nm (**Figure 2.8a**). As shown by SEM, this could be attributed to the flattening of the wrinkles (**Figure 2.8d-g**). These results suggest that both pillars and wrinkles contributed to the optical properties since both have periodicity in the micron scale. The hierarchical structure of tilted pillars on wrinkles greatly enhanced the film opaqueness while the straightened ones on wrinkles offered better color gratings than bare wrinkles.


Figure 2.8 (a) Transmission spectrum of a wrinkled PDMS film at various strains. Digital photograph of the sample at (b) 30% and (c) 0% strain. The boxes indicate the regions with pillars on top of wrinkles. Outside the boxes are regions with wrinkles only. SEM images of wrinkled PDMS pre-stretched at an angle of 60° to the pillar arrays and re-stretched to a strain of (d) 0%, (e) 10%, (f) 20%, and (g) 30%. Scale bars: 4 μ m.

2.6 Conclusions

We demonstrated a reversibly tunable optical window from tilted pillar arrays confined by mechanically induced wrinkles. We showed that the wrinkles undulated to accommodate the pillar pattern. Longer oxygen plasma treatment time increased the amplitude and periodicity of the wrinkles such that each wrinkle could accommodate two pillars, which tilting them in varying directions depending on the pre-stretch angle vs. lattice axis. The experimental observation was in agreement with finite element analysis. When mechanically stretched, the hierarchical film could reversibly 1) flatten the microwrinkles, 2) reduce the tilt of the pillars, 3) increase the pillar pitch, and thus, 4) offer a wide range of optical tunability from opaqueness (from tilted pillars) to grating color (from straight pillar array) to increasing transparency (from pillars at a larger pitch). Besides change of optical properties, we expect the fabricated hierarchical substrates to exhibit unique adhesion and wetting properties. The design of hierarchical surface structures demonstrated here offers a new concept to dynamically and dramatically change physical properties without altering materials' intrinsic properties. Further, the tunable patterns can be prepared from or coated with other functional materials, such as liquid crystal elastomers and gold, respectively, which will enhance responsiveness to other stimuli and recyclability.

2.7 Contributions

Lee, E., Zhang, M., Cho, Y., Cui, Y., Van der Spiegel, J., Engheta, N. and Yang, S. (2014), Tilted Pillars on Wrinkled Elastomers as a Reversibly Tunable Optical Window. Adv. Mater., 26: 4127–4133.

Lee, E. performed sample fabrication and characterization experiments. Zhang, M. performed FDTD modeling. Cho, Y. performed FEA modeling. Cui, Y. performed earlier experiments on the wrinkling of pillar structures, which inspired this study. Dr. Ertugrul Cubukcu and Jason Reed are acknowledged for access to and training for the optical characterization microscope.

2.8 References

- 1 Lee, E. *et al.* Tilted pillars on wrinkled elastomers as a reversibly tunable optical window. *Advanced Materials* **26**, 4127, doi:10.1002/adma.201400711 (2014).
- 2 Albert, J. D. *et al.* Suspended particle displays and materials for making the same. U.S. patent 6515649 (2003).

- 3 Sheraw, C. D. *et al.* Organic thin-film transistor-driven polymer-dispersed liquid crystal displays on flexible polymeric substrates. *Applied Physics Letters* **80**, 1088, doi:10.1063/1.1448659 (2002).
- 4 West, J. L. in *Liquid-crystalline polymers* Vol. 435 (eds R. A. Weiss & C. K. Ober) 475 (American Chemical Society, 1990).
- 5 Coates, D. Polymer-dispersed liquid crystals. *Journal of Materials Chemistry* **5**, 2063, doi:10.1039/jm9950502063 (1995).
- 6 Wang, J. Directly formed polymer dispersed liquid crystal light shutter displays. U.S. patent 5270843 (1993).
- 7 Drzaic, P. S. Polymer dispersed nematic liquid crystal for large area displays and light valves. *Journal of Applied Physics* **60**, 2142, doi:10.1063/1.337167 (1986).
- 8 Kim, H. *et al.* Structural colour printing using a magnetically tunable and lithographically fixable photonic crystal. *Nature Photonics* **3**, 534, doi:10.1038/Nphoton.2009.141 (2009).
- 9 Bechinger, C., Ferrere, S., Zaban, A., Sprague, J. & Gregg, B. A. Photoelectrochromic windows and displays. *Nature* **383**, 608, doi:10.1038/383608a0 (1996).
- 10 Parkin, I. P. & Manning, T. D. Intelligent thermochromic windows. J. Chem. Ed. **83**, 393, doi:10.1021/ed083p393 (2006).
- 11 Lampert, C. M. Electrochromic materials and devices for energy efficient windows. *Sol Energ Mat Sol C* **11**, 1, doi:10.1016/0165-1633(84)90024-8 (1984).
- 12 Lampert, C. M. Chromogenic smart materials. *Mater. Today* **7**, 28, doi:10.1016/S1369-7021(04)00123-3 (2004).
- 13 Lin, P.-C. & Yang, S. Mechanically switchable wetting on wrinkled elastomers with dual-scale roughness. *Soft Matter* **5**, 1011, doi:10.1039/B814145B (2009).
- 14 Lin, P.-C., Vajpayee, S., Jagota, A., Hui, C.-Y. & Yang, S. Mechanically tunable dry adhesive from wrinkled elastomers. *Soft Matter* **4**, 1830, doi:10.1039/B802848f (2008).
- 15 Vlasov, Y. A., O'Boyle, M., Hamann, H. F. & McNab, S. J. Active control of slow light on a chip with photonic crystal waveguides. *Nature* **438**, 65, doi:10.1038/nature04210 (2005).
- 16 Cattaneo, F. *et al.* Digitally tunable microfluidic optical fiber devices. *Journal Of Microelectromechanical Systems* **12**, 907, doi:10.1109/Jmems.2003.820285 (2003).
- 17 Park, W. & Lee, J.-B. Mechanically tunable photonic crystal structure. *Applied Physics Letters* **85**, 4845, doi:10.1063/1.1823019 (2004).
- 18 Zhu, X. *et al.* Two-dimensional photonic crystals with anisotropic unit cells imprinted from poly (dimethylsiloxane) membranes under elastic deformation. *Applied Physics Letters* **93**, 161911, doi:10.1063/1.3006061 (2008).
- 19 Arsenault, A. C. *et al.* From colour fingerprinting to the control of photoluminescence in elastic photonic crystals. *Nature Materials* **5**, 179, doi:10.1038/nmat1588 (2006).
- 20 Zhu, X., Wu, G., Dong, R., Chen, C.-M. & Yang, S. Capillarity induced instability in responsive hydrogel membranes with periodic hole array. *Soft Matter* **8**, 8088, doi:10.1039/C2sm25393c (2012).

- 21 Li, J. *et al.* Switching periodic membranes via pattern transformation and shape memory effect. *Soft Matter* **8**, 10322, doi:10.1039/C2sm25816a (2012).
- 22 Chandra, D., Yang, S., Soshinsky, A. A. & Gambogi, R. J. Biomimetic ultrathin whitening by capillary-force-induced random clustering of hydrogel micropillar arrays. *ACS Appl. Mater. Interfaces* **1**, 1698, doi:10.1021/am900253z (2009).
- 23 Izumi, M. *et al.* Changes in reflectin protein phosphorylation are associated with dynamic iridescence in squid. *Journal of The Royal Society Interface* **7**, 549, doi:10.1098/rsif.2009.0299 (2010).
- 24 Yoon, H. *et al.* Adhesion hysteresis of janus nanopillars fabricated by nanomolding and oblique metal deposition. *Nano Today* **4**, 385, doi:10.1016/j.nantod.2009.08.007 (2009).
- 25 Moon, M.-W., Cha, T.-G., Lee, K.-R., Vaziri, A. & Kim, H.-Y. Tilted janus polymer pillars. *Soft Matter* **6**, 3924, doi:10.1039/C0sm00126k (2010).
- 26 Reddy, S., Arzt, E. & del Campo, A. Bioinspired surfaces with switchable adhesion. *Advanced Materials* **19**, 3833, doi:10.1002/adma.200700733 (2007).
- 27 Chen, C.-M. & Yang, S. Directed water shedding on high-aspect-ratio shape memory polymer micropillar arrays. *Advanced Materials* **26**, doi: 10.1002/adma.201304030, doi:10.1002/adma.201304030 (2013).
- 28 Lee, S. G. *et al.* Switchable transparency and wetting of elastomeric smart windows. *Advanced Materials* **22**, 5013, doi:10.1002/adma.201002320 (2010).
- 29 Kang, S. M. *et al.* Robust superomniphobic surfaces with mushroom-like micropillar arrays. *Soft Matter* **8**, 8563, doi:10.1039/c2sm25879j (2012).
- 30 Xie, T., Xiao, X., Li, J. & Wang, R. Encoding localized strain history through wrinkle based structural colors. *Advanced Materials* **22**, 4390, doi:10.1002/adma.201002825 (2010).
- 31 Xu, H. *et al.* Deformable, programmable, and shape-memorizing micro-optics. *Advanced Functional Materials* **23**, 3299, doi:10.1002/adfm.201203396 (2013).
- 32 Zhang, Y., Lo, C.-W., Taylor, J. A. & Yang, S. Replica molding of high-aspectratio polymeric nanopillar arrays with high fidelity. *Langmuir* 22, 8595, doi:10.1021/la061372+ (2006).
- 33 Lin, P. C. & Yang, S. Spontaneous formation of one-dimensional ripples in transit to highly ordered two-dimensional herringbone structures through sequential and unequal biaxial mechanical stretching. *Applied Physics Letters* **90**, 241903, doi:10.1063/1.2743939 (2007).
- 34 Horcas, I. *et al.* Wsxm: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* **78**, 013705, doi:10.1063/1.2432410 (2007).
- 35 Hibbitt, H. Abaqus/epgen—a general purpose finite element code with emphasis on nonlinear applications. *Nuclear Engineering and Design* **77**, 271 (1984).
- 36 Bowden, N., Huck, W. T. S., Paul, K. E. & Whitesides, G. M. The controlled formation of ordered, sinusoidal structures by plasma oxidation of an elastomeric polymer. *Applied Physics Letters* **75**, 2557, doi:10.1063/1.125076 (1999).
- 37 Bowden, N., Brittain, S., Evans, A. G., Hutchinson, J. W. & Whitesides, G. M. Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer. *Nature* **393**, 146, doi:10.1038/30193 (1998).

- 38 Huang, J. *et al.* Capillary wrinkling of floating thin polymer films. *Science* **317**, 650, doi:10.1126/science.1144616 (2007).
- 39 Chung, J. Y., Nolte, A. J. & Stafford, C. M. Diffusion-controlled, self-organized growth of symmetric wrinkling patterns. *Advanced Materials* **21**, 1358, doi:10.1002/adma.200803209 (2009).
- 40 Stafford, C. M. *et al.* A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nature Materials* **3**, 545, doi:10.1038/nmat1175 (2004).
- 41 Chen, C. M. & Yang, S. Wrinkling instabilities in polymer films and their applications. *Polym. Int.* **61**, 1041, doi:10.1002/Pi.4223 (2012).
- 42 Guvendiren, M., Burdick, J. A. & Yang, S. Solvent induced transition from wrinkles to creases in thin film gels with depth-wise crosslinking gradients. *Soft Matter* **6**, 5795, doi:10.1039/C0sm00317d (2010).
- 43 Chen, C.-M., Reed, J. C. & Yang, S. Guided wrinkling in swollen, pre-patterned photoresist thin films with a crosslinking gradient. *Soft Matter* **9**, 11007, doi:10.1039/C3SM51881G (2013).
- 44 Cho, Y. *et al.* Study of architectural responses of 3d periodic cellular materials. *Model. Simul. Mater. Sci. Eng.* **21**, doi:10.1088/0965-0393/21/6/065018 (2013).

CHAPTER 3: A robust composite smart window for reversibly switching from high transparency to angle-independent structural color display

Adapted from:

Ge, D.,[†] Lee, E.,[†] Yang, L., Cho, Y., Li, M., Gianola, D. S. and Yang, S. (2015), A Robust Smart Window: Reversibly Switching from High Transparency to Angle-Independent Structural Color Display. Adv. Mater., 27: 2489–2495. ([†]Equal contribution.)¹ Reproduced with permission.

3.1 Introduction

Commercial buildings alone account for nearly 40% of the total energy consumption in the U.S. Among them, electricity is the largest energy source for buildings. Therefore, the design of new energy efficient materials and technologies is crucial to meet goals such as the Net-Zero Energy Commercial Building Initiative (CBI) put forward by the U.S. Department of Energy (DOE). There has been tremendous interest in economizing energy uses in buildings through house roofing, skylights, and architectural windows.²⁻⁴ For example, smart windows have been developed, which become opaque to block or reflect sunlight on scorching days to save air conditioning costs, and return to a transparent state at a low lighting condition to improve light harvesting and capture free heat from the sun.^{2,5-7} Typically, optical-modulation in window or coating materials is realized through an external stimuli-triggered switch in chemistry and/or morphology to produce a change in optical properties, including the use of suspended particles,⁸ polymer dispersed liquid crystals (PDLCs),⁹⁻¹³ and chromogenic

materials driven by ion and electron insertion/extraction, light,⁶ temperature,¹⁴ and electrical field.¹⁵ The assembly of the device is often complex, and many of the components are chemically unstable and costly. Therefore, facile material handling and fabrication is desirable for large-area smart windows with switchable optical properties.

Structural color resulting from the interference, diffraction and scattering of light from micro- or nano-structures with lengths scales on the order of the wavelength of light¹⁶⁻¹⁸ offers a promising alternative to dynamically tune the optical properties of materials in response to external stimuli without changing their bulk properties.¹⁶⁻¹⁸ In nature, bio-organisms switch color /opaqueness and/or transparency to suit the local environment for hiding from the predators, for signaling, or for mating purposes.¹⁹⁻²² For example, squids and octopus in deep sea are masters of disguise. They are normally transparent in sea, thus invisible to a predatory fish in down-welling light. They can quickly turn into red, however, thus become invisible again to fish with bioluminescent searchlights.²³ They alternate the body color by stretching the skin to enlarge the embedded chromophores.²⁴

Mechanical modulation is a common practice to control light transmission macroscopically, such as the opening and closing of curtains and blinds. However, mechanical driving of macroscopic units is cumbersome and they must communicate through a mainframe. It is highly desirable to develop a skin-like material/device that can be integrated into building components to change transparency or color. At the microand nanoscales, tuning of the optical properties by mechanical stretching and compressing has been demonstrated from patterned polymer thin films, including micro-²⁵ and nanopillar arrays²⁶ on wrinkled polydimethylsiloxane (PDMS), shape memory polymers consisting of periodic microhole arrays²⁷ and micro-optic components.²⁸ Many of these devices have inherent, angle-dependent structural color due to Bragg diffraction from the periodic structures. Typically, the initial state is opaque or colored, attributed to the pre-existing micro-/nanostructures. The windows exhibit increased transmission upon stretching due to the reduction of surface roughness, thus less scattering. However, the roughness of the materials and the resulting light scattering cannot be completely eliminated. Therefore, it is difficult to achieve high transparency with >90% transmittance in the visible region either before or after mechanical modulation.

Here, we prepare a composite film consisting of a thin layer of quasi-amorphous array of silica nanoparticles (NPs) embedded in bulk elastomeric PDMS. Importantly, it is highly transparent (>90% transmittance in the visible wavelength) in the initial state. Upon mechanical stretching, the transmittance is dramatically reduced to 30% and display angle-independent structural color at a strain >40%. The color can be tuned by the silica NP size. Unlike the silica NPs/PDMS films prepared from highly ordered silica colloidal crystals,²⁹ the reflective color is invariant with increased strain. The switch between transparency and colored states can be reversibly cycled at least 1000 times without losing the film's structural and optical integrity.

3.2 Experimental methods

3.2.1 Materials

Silica (SiO₂) NPs with diameter of 221 nm, 258 nm and 306 nm were synthesized by Stöber method.^[9,10] The polydispersity of the silica NPs was less than 8%. Dow Corning Sylgard 184 silicone elastomer kit was used for preparing PDMS.

3.2.2 Fabrication of the hybrid window

SiO₂ NPs were dispersed into isopropanol (99.8%, Fisher Scientific Inc.) at 10 wt% and ultrasonicated for 2 h (Branson Ultrasonic Cleaner, 2210) to prepare the spray solutions. The spray solution was loaded into an airbrush with nozzle size of 0.2 mm (Master Airbrush Model G44) and the operating pressure was 50 kPa. The solution was sprayed 4 times on the polystyrene (PS) petri dish at a spray distance of 5 cm and a moving speed of ~5 cm/s. Dow Corning Sylgard 184 silicone elastomer and curing agent were mixed at a weight ratio 10:1. After degassing, the PDMS precursor was cast on the sprayed PS petri dish, and infiltrated into the voids of the silica NP film. The thickness of the PDMS film was controlled from 0.5 mm to 1 mm. The whole setup was then cured at 65°C for 4 h. Finally, the hybrid film was carefully peeled from the PS petri dish for stretching.

3.2.3 Fabrication of the smart window with embedded letters

A solid mask of "PENN" and a hollow mask of "N" were prepared from cut paper. The mask was placed on the petri dish, followed by spray coating of silica NPs. After removal of the mask, PDMS precursor was cast on the petri dishes following the same procedure to fabricate the hybrid window described above.

3.2.4 Sample characterization

Scanning electron microscopy (SEM) images were taken by FEI Quanta Field Emission Gun Environmental SEM in high vacuum mode at an acceleration voltage of 5kV. The reflectance and scattering spectra at various strains and angles, and the time-dependent transmittance were collected from a USB4000 fiber optical spectrometer (Ocean Optics) combined with a custom-built stretcher and angle-resolved stage. Transmittance of the smart windows at various strains was measured using the Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies) combined with a custom-built stretcher. Optical images were taken by optical microscopy (BX 61, Olympus) in reflection and transmission modes. *In situ* confocal microscopy was performed using a laser scanning confocal microscope (Thorlabs, Inc.) in reflection mode using a 635nm laser source. Mechanical testing using this imaging modality was performed using a custom-built microtensile testing apparatus.

3.2.5 Finite-element analysis

The finite element analyses were performed using the implicit finite element software ABAQUS/Standard (Dassault Systèmes Americas Corp., Waltham, MA). The materials were linear elastic with properties chosen to match the silica (Young's modulus = 73 GPa, Poisson's ratio = 0.17) and the PDMS (Young's modulus = 0.75 MPa, Poisson's ratio = 0.49). The 3-dimensional continuum element, C3D4, was adopted with the characteristic element length of 5 nm. The adhesive contact between the spherical silica particle and the PDMS matrix was considered based on the linear elastic traction-separation model, which assumes initially linear elastic behavior followed by the initiation and evolution of damage. The elastic adhesive behavior is represented by an elastic constitutive matrix, which relates the normal and shear stresses to the normal and shear separations across the contact interface.

$$\boldsymbol{\sigma} = \begin{cases} \sigma_{n} \\ \sigma_{s} \\ \sigma_{t} \end{cases} = \begin{bmatrix} K_{nn} & K_{ns} & K_{nt} \\ K_{ns} & K_{ss} & K_{st} \\ K_{nt} & K_{st} & K_{tt} \end{bmatrix} \begin{cases} \delta_{n} \\ \delta_{s} \\ \delta_{t} \end{cases} = \mathbf{K} \boldsymbol{\delta}$$
(3-1)

where the nominal traction stress, σ , has three components along the normal (n) and two shear (s and t) directions. **K** is the elastic constitutive matrix and δ is the corresponding separations. For simplification, we assumed that the normal and tangential stiffness components are not coupled. Then, the terms K_{nn}, K_{ss}, and K_{tt} determine the uncoupled traction-separation behavior on the contact interface.

3.3 Window fabrication and actuation

The fabrication of the smart window is illustrated in **Figure 3.1a**. First, the silica NP solution was spray-coated onto a polystyrene substrate following the procedure reported earlier to create superhydrophobic, angle-independent color coatings from quasi-amorphous NP arrays.³⁰ Here, angle-independent blue, green, and pink films (**Figure 3.1b**) were obtained from silica NPs with diameters of 221 nm, 258 nm, and 306 nm, respectively. As shown in scanning electron microscopy (SEM) images, the particles formed quasi-amorphous arrays with short-range ordering yet were long-range disordered (**Figure 3.1c**), in agreement with our prior observation.³⁰ PDMS precursor solution was then cast over the NP film, filling the voids between the particles. Since the refractive index of PDMS (1.425 at 632.8 nm)³¹ is very close to that of silica (1.457 at 632.8 nm),³² the composite films were highly transparent in the visible and near infrared (vis-NIR) range, as seen in **Figure 3.1d**. Indeed, it is difficult to discern the PDMS films with and without embedded silica NPs.



Figure 3.1 (a) Schematic of the smart window fabrication process. (b) Digital photographs of the nanoparticle films prepared with nanoparticles of diameter (i) 221, (ii) 258, and (iii) 306nm. (c) SEM image of nanoparticle film showing quasi-amorphous ordering. (d) Digital photograph and (e) SEM image of the highly transparent silica/PDMS composite film. (f) Digital photographs of stretched silica/PDMS films with embedded nanoparticles of diameter (i) 221, (ii) 258, and (iii) 306nm, respectively.

Under SEM, it could be seen that the films had two layers: a thin layer of hard silica NP/PDMS composite (4-5 μ m thick) and a bulk layer of pure PDMS (**Figure 3.1e**). The thickness of the pure PDMS layer ranged from 0.5-1 mm depending on the amount of PDMS solution used in casting. Close-packed silica NP films were also prepared for comparison. The latter tended to rupture easily at the interface between the composite layer and the pure PDMS layer when peeled off from the supporting substrate due to the narrow PDMS ligments (<20 nm)³³ between the close-packed silica NPs. In comparison, the quasi-amorphous structure of spray-coated NP films possessed rather random, thus larger pores from place to place to infiltrate PDMS. The resulting thicker PDMS layers between the silica NPs offered much higher mechanical strength against macroscopic rupture. Upon stretching, two optical phenomena were observed: 1) switching from

transparency to opacity, and 2) appearance of uniform, angle-independent reflective color, blue, green, and yellow-white from the films with silica NPs of diameter 221 nm, 258 nm, and 306 nm, respectively (**Figure 3.1f**). These phenomena are reversible upon release of the strains.

3.4 Morphology characterization

To investigate the origin of these phenomena, which have not been reported in the literature, we used optical microscopy and SEM to monitor the silica NP/PDMS films stretched at various strains (**Figure 3.2a-b**). As seen with optical microscopy in reflectance mode (**Figure 3.2a**), microcracks began to appear (**Figure 3.2a_ii**) when the strain level reached 20%. With further increase of strain, the number and length of microcracks increased and wrinkling began to occur transverse to the applied strain with wavelength of ~ 25 μ m (**Figure 3.2a_iii**). The wrinkle formation can be explained by the mismatch of mechanical properties of the bilayer structure of the silica NP/PDMS composite film.³⁴ In addition, the optical micrographs taken in reflection mode showed that color appeared randomly in the film. Since the inside of the composite layer could not be imaged clearly under reflection mode, transmission mode was used to image the film instead (**Figure 3.2b**). **Figure 3.2b_iii-iv** showed that the whole film was yellow/purple-ish, complementary to the reflective color of blue and green seen in **Figure 3.1f_ii** under transmission mode.

However, surface wrinkles and microcracks are not the only reasons contributed to the displayed color. Nanosized voids were also observed from the cross-sectional SEM of the composite film under ~40% strain (**Figure 3.2c**), and PDMS ligaments between the particles were highly stretched, while the silica NPs remained embedded. Voids tended to form locally in high stress regions, rather than across the whole film. To better image the in-plane structure of the composite film and the formation of the voids under mechanical strain, we fabricated a PDMS film dispersed with silica particles of larger diameter, 5μ m, and imaged the film before and after stretching using confocal microscopy. As seen in **Figure 3.2d**, microvoids were formed on both sides of the silica microparticles parallel to the stretching direction. It is known that PDMS can detach easily from the silica particles because of the low adhesion force (~10 kPa) between PDMS (hydrophobic) and untreated silica (hydrophilic).^{35,36} When the strain is released, the voids are closed and this process can be reversibly repeated.



Figure 3.2 Optical micrographs of a silica/PDMS film consisting of nanoparticles of diameter 258 nm at various strains in (a) reflection and (b) transmission modes (Scale bars: 20 μ m). (c) SEM image of a stretched silica/PDMS film with nanoparticles of diameter 258 nm at ~ 80% strain. Arrows indicate PDMS ligaments. (d) Confocal optical micrograph of an (i) un-stretched and (ii) a stretched silica nanoparticle (diameter of 5 μ m)/PDMS film. Circles indicate silica nanoparticles. Black regions indicate the voids.

3.5 Optical response

With knowledge of the film morphology under various strains, the transmittance of the film was investigated using UV-vis-NIR spectroscopy. By naked eyes, the transparent, as-prepared silica NP/PDMS film began to look translucent at about 20% strain and was completely opaque at about 100% strain (**Figure 3.3a**). The transmittance is dependent on the size of the silica NPs and thus, the resulting voids from mechanical

strain (**Figure 3.3b-d**). Smaller particles (221 nm in diameter) and voids have low transmittance at shorter wavelengths due to Rayleigh scattering, which is wavelength-dependent. Larger particles (258 and 306 nm in diameters) and voids mainly have Mie scattering, which is wavelength-independent.



Figure 3.3 (a) Digital photographs of a silica/PDMS film consisting of nanoparticles of diameter 258 nm at various strains. Transmission spectra of silica nanoparticle/PDMS composite films at various strains. The silica nanoparticles have diameters of (b) 221 nm, (c) 258 nm, and (d) 306 nm.

The strain-transmittance curves (**Figure 3.4a**) showed three stages, corresponding to wrinkle and crack formation at 0-20% strain level, void formation at 20-80% strain level, and leveling-off at >80% strain, in agreement with observation from optical microscopy shown in **Figure 3.2a-b**. The transmittance decreased the most at the void formation stage, suggesting that void formation was mainly responsible for the transparency change in our smart window. The average transmittance in the visible wavelength range (400-700 nm) of the as-prepared silica NP/PDMS film and a pure PDMS film were measured to be ~92% and ~94%, respectively (**Figure 3.4b**). When stretched, a significantly large drop in the transmittance of the silica NP/PDMS film in the visible region was observed (**Figure 3.4b**): over 50% in average for different particle sizes and the largest change was nearly 70%, much higher than those reported in literature.^{25,26}

To demonstrate repeatability and robustness of our smart window, we stretched and released the films from 20% to 70% strain at a frequency of 0.5 Hz for 1000 times, and the transparency was measured continuously at 500 nm. The transmittance of the films after stretching and releasing 1000 times was nearly identical to that of the unstretched film (**Figure 3.4b** inset). We believe that the durability and stability of the films can be attributed to the combination of thick PDMS layer (0.5-1 mm) and thin silica NP/PDMS composite layer (~4-5 μ m). While the top thin layer is responsible for color/transmittance change, the bottom thick PDMS layer produces necessary restoring force for the entire film for repeated stretching and release. Meanwhile, the elastic PDMS nanoscale ligaments generated during stretching in the composite layer (**Figure 3.2c**) played a role to confine the silica NPs in their local regions, where color appeared and intensified upon stretching but did not change for a given NP size.



Figure 3.4 (b) Transmittance spectra of a pure PDMS film (black), an as-prepared silica nanoparticle/PDMS film (green), and a silica nanoparticle/PDMS film stretched at 100% strain (blue) and released (red) 1000 times. Inset: Transmittance change as a function of stretching/release cycles. (c) Transmittance vs. strain at wavelengths of 500 nm and 700 nm, respectively. (d) Reflectance spectra of the composite film with nanoparticle

diameter of 258 nm at various strains at a viewing angle of 10° . Inset: schematic illustration of the viewing angle in the experimental setup. (e) Reflectance spectra of silica nanoparticle/PDMS films with 80% strain at a viewing angle of 10° . The nanoparticles have diameters of (i) 221, (ii) 258, and (iii) 306 nm, respectively. Inset: optical micrographs of the stretched silica/PDMS membrane with nanoparticles of diameter of (i) 221, (ii) 258, and (iii) 306 nm, respectively. Scale bars: 20 µm. (f) Reflectance spectra of the composite film with nanoparticle diameter of 258 nm with 80% strain at various viewing angles.

To characterize the color of the smart windows, we measured the reflectance of the films at different strain levels in the vis-NIR range using a custom-built spectrophotometer outfitted with a reflectance and backscattering optical fiber (Ocean Optics), as shown in the Figure 3d inset. Reflectance peaks started to appear at 40% strain and intensified at strains >60% (Figure 3.4c), which matched the formation of microwrinkles and nanovoids shown in **Figure 3.2**. The peak position did not noticeably change with increase of strain. We should note that the color of the silica NP/PDMS film (Figure 3.1f and Figure 3.4d), however, is different from that of quasi-amorphous silica NP array (Figure 3.1b and Figure 3.4e) of the same NP size. As seen in Figure 3.4e, the reflectance peaks (λ_R) of the silica NP arrays were dependent on the size of NPs, in agreement with literature:^{37,38} blue (NP diameter, 221 nm), green (258 nm) and pink (306 nm) films had reflectance peaks at 461 nm, 517 nm, 625 nm, respectively. At 80% strain and a viewing angle of 10° , the reflectance peaks of the films prepared with 221 nm, 258 nm, and 306 nm silica NPs were at wavelengths 454 nm, 501 nm, and 587 nm, respectively (Figure 3.4d). The reflectance peaks of the stretched silica NP/PDMS films were blue-shifted compared to pure NP films of the same NP size, but there was no further change of peak position at various strains. We then tilted the films with respect to the detector. As seen in Figure 3.4f, the reflectance peak positions did not change with

the viewing angles, characteristic of quasi-amorphous structural color. Instead, the reflectance peak intensity is dependent on the viewing angle and maximized at a viewing angle of 10°. In contrast, optically switchable windows reported in literature typically produce angle-dependent color due to Bragg diffraction of the highly-ordered structures.^{25,28}

3.6 Mechanism

Based on our observations and measurements, we proposed a mechanism of void formation in **Figure 3.5**, where the changes in the optical properties could be attributed to the microstructural change, including micro-roughness from wrinkles and nano-voids formed between PDMS and silica NPs (**Figure 3.2a-b**). The void formation led to new reflection interfaces (i.e. void/silica, void/PDMS, **Figure 3.2c-d**) and a dramatic increase (over 200 times) in the reflectance at the interface and thus, a significant drop in transparency. The reflectance at the interface between two media under the normal incident light is given by

$$R = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}$$
(3-2)

where n_1 and n_2 are the refractive indices of media 1 and media 2. As seen in **Figure 3.5**, there were three interfaces in the stretched silica/PDMS composite film: silica/PDMS interface, silica/void interface, and PDMS/void interface. Here, $n_{\text{silica}}=1.457$ at 632.8nm, $n_{\text{PDMS}} = 1.423$ at 632.8nm, $n_{\text{void}} = 1$. The reflectance at the interfaces is $R_{\text{silica/PDMS}} =$

0.014%, $R_{\text{silica-void}} = 3.46\%$, and $R_{\text{PDMS-void}} = 3.05\%$. This greater than 200-fold increase in reflectance resulted in the observed color and drop in transmittance.



Figure 3.5 Schematic illustration of the void formation around the silica particles when stretched. Arrows indicate PDMS ligaments.

To support our hypothesis, finite element simulation (**Figure 3.6**) was performed to better understand the adhesive contact between the silica particle and the PDMS matrix. The stretching of a silica particle embedded in PDMS was simulated based on the concept of a representative unit structure, defined in **Figure 3.6a**. The adhesive terms K_{nn} , K_{ss} , and K_{tt} determine the uncoupled traction-separation behavior on the contact interface. For simulated adhesive contact terms ranging three orders of magnitude, it was shown that void formation on either side of the silica particle parallel to the stretching direction is possible (**Figure 3.6b-d**).



Figure 3.6 Finite element simulation. (a) Cross-section of the unit structure (275 x 275 nm) consisting of PDMS (gray) with a spherical silica nanoparticle of diameter 250 nm (blue). Predicted void formation where the adhesive contact terms $K_{nn} = K_{ss} = K_{tt} = (b) 1.0$ MPa, (c) 10.0 MPa, and (d) 100.0 MPa.

Mechanical strain causes the thinning of the silica NP/PDMS composite film due to the positive Poisson's ratio of PDMS, 0.5. Since the top layer of silica NP/PDMS is much thinner than the bottom PDMS bulk layer, the thinning of the composite film should mainly occur in the bulk PDMS layer. Thus, the interplanar spacing (d_{planar}) of NP assembly should not change much with the strain, while the location of voids should correlate to the silica NP positions (**Figure 3.2c-d**). The void arrangements formed locally should also be quasi-amorphous, analogous to the quasi-amorphous silica NP arrays, which were somewhat locked by the adjacent PDMS layer. Thus, the angleindependent structural color of the stretched films should be the result of the quasiamorphous structures consisting of voids and silica NPs. As mentioned earlier, voids occurred locally at the high stress positions, and the local strain, obtained from the SEM images (**Figure 3.2c**), was on the order of 100% even at a relatively low global strain level. To explain this, the local volume filling fraction of voids was calculated as follows.

Typically, the reflection peaks λ_R of colloidal crystals are angle dependent and can be explained by the Bragg-Snell law:

$$\lambda_R = 2d_{planar} \left(n_{eff}^2 - \sin^2 \theta \right)^{\frac{1}{2}}$$
(3-3)

where d_{planar} is the interplanar spacing, n_{eff} is the effective refractive index, and θ is the incidental angle. However, the reflection peaks of quasi-amorphous arrays of

nanoparticles are angle-independent. According to the data fitting in a previous study,³⁷ the reflection peaks λ_R of quasi-amorphous arrays are linearly proportional to the silica nanoparticle size (D_{silica}) and can be calculated as:

$$\lambda_R = a \, D_{silica} = 2d_{planar} n_{eff} \tag{3-4}$$

Taking $\theta = 0^{\circ}$ in Equation (3-3), we obtained the factor *a* as 2.04 for quasi-amorphous nanoparticle arrays, and 2.18 for face-centered cubic (FCC) colloidal crystals.

For the pure silica nanoparticle arrays, the effective refractive index n_{eff} is

$$n_{eff} = f_{silica} n_{silica} + f_{air} n_{air}$$
(3-5)

where *f* is the volume filling fraction. Here, $f_{silica} + f_{air} = 1$, $n_{silica} = 1.457$ and $n_{air} = 1$, so

$$\lambda_R = 2d_{planar}(1.457 - 0.457f_{air}) \tag{3-6}$$

For the silica nanoparticle/PDMS composite layer, n_{eff} is

$$n_{eff} = f_{PDMS} n_{PDMS} + f_{silica} n_{silica} + f_{void} n_{void}$$
(3-7)

The ratio of the volume filling fraction of the sprayed quasi-amorphous particle array to PDMS is f_{silica} : $f_{PDMS} = 0.35:0.65$.³⁷ Here $f_{silica} + f_{PDMS} + f_{void} = 1$, $n_{silica} = 1.457$, $n_{PDMS} = 1.423$ and $n_{void} = n_{air} = 1$, so

$$\lambda_R = 2d_{planar} \left(1.445 - 0.445 f_{void} \right) \tag{3-8}$$



Figure 3.7 (a) Schematic of a stretched silica/PDMS composite film with a single particle. (b) The relationship of strain and volume filling fraction of void.

The void volume filling fraction (f_{void}) can be estimated based on the model. Here, the void is assumed as a perfect ellipsoid and a silica particle is embedded in the void (**Figure 3.7a**). So the volume of void is

$$V_{void} = \frac{4}{3}\pi ar^2 - \frac{4}{3}\pi r^3 = \frac{(a-r)}{r}V_{silica}$$
(3-9)

The void volume filling fraction is

$$f_{void} = \frac{V_{void}}{V_{void} + V_{silica} + V_{PDMS}}$$
(3-10)

Particles are near close-packed, so the edge PDMS thickness (*b*) is very small comparing to the particle diameter. Here *b* is ignored, the strain is $\varepsilon = (a-r)/r$ and V_{PDMS} : $V_{silica} = 0.65:0.35$. Therefore,

$$f_{void} = \frac{0.65\,\varepsilon}{0.65\,\varepsilon + 1} \tag{3-11}$$

The ε - f_{void} curve is shown in **Figure 3.7b**. When the strain is greater than 80%, f_{void} is greater than $f_{air} = 0.35$.

These results suggest that the local strain applied to the thin NP/PDMS layer is not equivalent to the global strain applied to the whole film; cracking/wrinkling and nanovoids occur to relax the local strain despite the continuing straining of the bulk PDMS layer. Therefore, the reflection peak position did not change with the increase of applied strain, while the peak intensity increased (**Figure 3.4c**) due to the increase in the number of voids. Likewise, blue-shift of the reflection peaks of stretched silica NP/PDMS film vs. the as-prepared silica NP arrays can be explained by the decrease of d_{planar} and increase of f_{void} according to Equation (3-8).

In addition to being a light blocking smart window or a scattering surface for projectors, the composite film can also be used in display and security applications. Positive or negative letters can be embedded in the composite films by spray coating of silica NPs on different masks, followed by mask removal and PDMS casting. As seen in **Figure 3.8**, hidden letters "PENN" (negative) and "N" (positive) can be reversible revealed upon stretching and releasing of the film.



Figure 3.8 Reversibly revealing and hiding the letters patterned within the silica nanoparticle/PDMS film under mechanical stretching and releasing.

3.7 Conclusions

In summary, we presented a smart optical window that could be reversibly switched from a highly transparent state (90% transmittance in the visible region) to opaqueness (30% transmittance) and display angle-independent reflective colors through mechanical stretching and release. The window was a bilayer elastomeric film consisting of a thin, hard layer of quasi-amorphous silica NP/PDMS and a thick, elastomeric layer of bulk PDMS. The displayed colors were found dependent only on the NP size not the stretching strain, although they blue-shifted compared to the films prepared from NPs only. The dramatic change of optical responses is attributed to an increase of diffused light scattering and absorption resulting from the formation of microwrinkles and voids during stretching. The design of composite structures demonstrated here offers a facile and low cost approach to dynamically and dramatically change optical properties. Compared to smart windows reported in literature, ours have several unique characteristics, including: 1) The initial state is truly transparent due to refractive index match between silica NPs and PDMS, whereas most smart windows are opaque or colored in the original state; 2) The change of transmittance in the vis-NIR region is very large, $\sim 60\%$; 3) The sprayed NPs are quasi-amorphous, therefore, much more robust against stretching in comparison to highly ordered colloidal crystals. They offer angleindependent color display upon stretching whereas most stretchable smart windows display angle-dependent colors; 4) The displayed color is independent of stretching strain, but dependent on NP size; 5) The film is highly robust in repeated stretching and releasing (at least 1000 cycles) since the majority of the film under strain is the bulk PDMS layer. Although smart windows are demonstrated here for light transmission control, they can also be used in applications such as displays, camouflages, and security, as well as heat/solar gain control. The material design presented here offers new insights to dynamically and dramatically change physical properties. Further, the concept presented here can be applied to other functional material systems, such as liquid crystal elastomers and shape memory polymers, to design highly responsive, nano-/micro-structured materials that are sensitive to heat, light and moisture.

3.8 Contributions

Ge, D.,[†] Lee, E.,[†] Yang, L., Cho, Y., Li, M., Gianola, D. S. and Yang, S. (2015), A Robust Smart Window: Reversibly Switching from High Transparency to Angle-Independent Structural Color Display. Adv. Mater., 27: 2489–2495. ([†]Equal contribution.)

Ge, D. and Lee, E. performed sample fabrication and characterization. Yang, L. participated in discussion and provided physical insights of experiments. Cho, Y. provided theoretical insights through FEA modeling. Li, M. performed confocal optical microscopy characterization.

3.9 References

- 1 Ge, D. *et al.* A robust smart window: Reversibly switching from high transparency to angle-independent structural color display. *Advanced Materials* **27**, 2489, doi:10.1002/adma.201500281 (2015).
- 2 Debije, M. G. Solar energy collectors with tunable transmission. *Advanced Functional Materials* **20**, 1498, doi:10.1002/adfm.200902403 (2010).
- 3 Gutierrez, M. P. & Lee, L. P. Multiscale design and integration of sustainable building functions. *Science* **341**, 247, doi:10.1126/science.1237278 (2013).
- 4 Gutierrez, M. P. & Zohdi, T. I. Effective reflectivity and heat generation in sucrose and pmma mixtures. *Energy Build.* **71**, 95, doi:10.1016/j.enbuild.2013.11.046 (2014).
- 5 Cupelli, D. *et al.* Self-adjusting smart windows based on polymer-dispersed liquid crystals. *Sol Energ Mat Sol C* **93**, 2008, doi:10.1016/j.solmat.2009.08.002 (2009).
- 6 Bechinger, C., Ferrere, S., Zaban, A., Sprague, J. & Gregg, B. A. Photoelectrochromic windows and displays. *Nature* **383**, 608, doi:10.1038/383608a0 (1996).
- 7 Baetens, R., Jelle, B. P. & Gustavsen, A. Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: A state-of-the-art review. *Sol Energ Mat Sol C* **94**, 87, doi:10.1016/j.solmat.2009.08.021 (2010).
- 8 Albert, J. D. *et al.* Suspended particle displays and materials for making the same. U.S. patent 6515649 (2003).
- 9 Sheraw, C. *et al.* Organic thin-film transistor-driven polymer-dispersed liquid crystal displays on flexible polymeric substrates. *Applied Physics Letters* **80**, 1088, doi:10.1063/1.1448659 (2002).
- 10 West, J. L. in *Liquid-crystalline polymers* Vol. 435 (eds R. A. Weiss & C. K. Ober) 475 (American Chemical Society, 1990).
- 11 Coates, D. Polymer-dispersed liquid crystals. J. Mater. Chem. 5, 2063 (1995).
- 12 Wang, J. Directly formed polymer dispersed liquid crystal light shutter displays. U.S. patent 5270843 (1993).
- 13 Drzaic, P. S. Polymer dispersed nematic liquid crystal for large area displays and light valves. *J. Appl. Phys.* **60**, 2142 (1986).
- 14 Parkin, I. P. & Manning, T. D. Intelligent thermochromic windows. *J. Chem. Ed.* **83**, 393 (2006).
- 15 Lampert, C. M. Electrochromic materials and devices for energy efficient windows. *Solar Energy Mater.* **11**, 1, doi:10.1016/0165-1633(84)90024-8 (1984).
- 16 Kinoshita, S. & Yoshioka, S. Structural colors in nature: The role of regularity and irregularity in the structure. *ChemPhysChem* 6, 1442, doi:10.1002/cphc.200500007 (2005).
- 17 Vukusic, P. & Sambles, J. R. Photonic structures in biology. *Nature* **424**, 852, doi:10.1038/nature01941 (2003).
- 18 Srinivasarao, M. Nano-optics in the biological world: Beetles, butterflies, birds, and moths. *Chem Rev* **99**, 1935, doi:10.1021/cr970080y (1999).

- 19 Liu, F., Dong, B. Q., Liu, X. H., Zheng, Y. M. & Zi, J. Structural color change in longhorn beetles tmesisternus isabellae. *Opt Express* 17, 16183, doi:10.1364/OE.17.016183 (2009).
- 20 Stavenga, D. G., Leertouwer, H. L., Marshall, N. J. & Osorio, D. Dramatic colour changes in a bird of paradise caused by uniquely structured breast feather barbules. *P Roy Soc B-Biol Sci*, doi:10.1098/rspb.2010.2293 (2010).
- 21 Holt, A. L., Sweeney, A. M., Johnsen, S. & Morse, D. E. A highly distributed bragg stack with unique geometry provides effective camouflage for loliginid squid eyes. *Journal of The Royal Society Interface* **8**, 1386, doi:10.1098/rsif.2010.0702 (2011).
- 22 Potyrailo, R. A. *et al.* Morpho butterfly wing scales demonstrate highly selective vapour response. *Nature Photonics* **1**, 123, doi:10.1038/nphoton.2007.2 (2007).
- 23 Zylinski, S. & Johnsen, S. Mesopelagic cephalopods switch between transparency and pigmentation to optimize camouflage in the deep. *Curr Biol* **21**, 1937, doi:10.1016/j.cub.2011.10.014 (2011).
- 24 Izumi, M. *et al.* Changes in reflectin protein phosphorylation are associated with dynamic iridescence in squid. *Journal of The Royal Society Interface* **7**, 549, doi:10.1098/rsif.2009.0299 (2010).
- Lee, E. *et al.* Tilted pillars on wrinkled elastomers as a reversibly tunable optical window. *Advanced Materials* **26**, 4127, doi:10.1002/adma.201400711 (2014).
- Lee, S. G. *et al.* Switchable transparency and wetting of elastomeric smart windows. *Advanced Materials* **22**, 5013, doi:10.1002/adma.201002320 (2010).
- 27 Li, J. *et al.* Switching periodic membranes via pattern transformation and shape memory effect. *Soft Matter* **8**, 10322, doi:10.1039/C2sm25816a (2012).
- 28 Xu, H. *et al.* Deformable, programmable, and shape-memorizing micro-optics. *Advanced Functional Materials* **23**, 3299, doi:10.1002/adfm.201203396 (2013).
- 29 Fudouzi, H. & Sawada, T. Photonic rubber sheets with tunable color by elastic deformation. *Langmuir* **22**, 1365, doi:10.1021/la0521037 (2005).
- 30 Ge, D., Yang, L., Wu, G. & Yang, S. Spray coating of superhydrophobic and angle-independent coloured films. *Chem Commun* **50**, 2469, doi:10.1039/C3CC48962K (2014).
- 31 Raman, K., Murthy, T. R. S. & Hegde, G. M. Fabrication of refractive index tunable polydimethylsiloxane photonic crystal for biosensor application. *Phys Proc* **19**, 146, doi:10.1016/j.phpro.2011.06.139 (2011).
- 32 Malitson, I. H. Interspecimen comparison of the refractive index of fused silica. *J Opt Soc Am* **55**, 1205, doi:10.1364/josa.55.001205 (1965).
- 33 Ge, D. T. *et al.* Reflective behavior of strong absorption metallic photonic crystals. *Synthetic Metals* **161**, 235, doi:10.1016/j.synthmet.2010.11.025 (2011).
- 34 Yang, S., Khare, K. & Lin, P.-C. Harnessing surface wrinkle patterns in soft matter. *Advanced Functional Materials* **20**, 2550, doi:10.1002/adfm.201000034 (2010).
- 35 Chau, K. *et al.* Dependence of the quality of adhesion between poly(dimethylsiloxane) and glass surfaces on the composition of the oxidizing plasma. *Microfluid Nanofluid* **10**, 907, doi:10.1007/s10404-010-0724-y (2011).

- 36 Millare, B. *et al.* Dependence of the quality of adhesion between poly(dimethylsiloxane) and glass surfaces on the conditions of treatment with oxygen plasma. *Langmuir* **24**, 13218, doi:10.1021/la801965s (2008).
- 37 Ge, D., Yang, L., Wu, G. & Yang, S. Angle-independent colours from spray coated quasi-amorphous arrays of nanoparticles: Combination of constructive interference and rayleigh scattering. *Journal of Materials Chemistry* **2**, 4395, doi:10.1039/C4TC00063C (2014).
- 38 Takeoka, Y. *et al.* Production of colored pigments with amorphous arrays of black and white colloidal particles. *Angewandte Chemie International Edition* **52**, 7261, doi:10.1002/anie.201301321 (2013).

CHAPTER 4: Directing highly uniform molecular alignment in liquid crystal elastomer micropillar arrays through interplay of interfacial chemistry and topography

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4.1 Introduction

Because of their geometrical, mechanical, and electronic anisotropy, liquid crystal (LC) molecules are not only highly sensitive to external aligning fields but can also exquisitely control the propagation of electromagnetic phenomena. Consequently, LC molecules have long been of interest for scientific advancement and technological applications, including display, artificial muscles and actuators that rely on anisotropic properties of LC molecules.¹⁻⁴ It is known that nematic liquid crystalline elastomers (NLCEs) exhibit a spontaneous contraction along the director axis when heated above their nematic (N) to isotropic (I) phase-transition temperatures (T_{NI}), and the polymer chains change to a spherical conformation.⁵ Therefore, NLCEs have a reversible shape memory effect when triggered by external stimuli, including heat, UV light and electric field.⁶⁻¹⁰ However, the deformation of LCE networks is highly dependent on the molecular alignment of LC molecules, both globally and locally, depending on the boundary conditions at interfaces, including topology and surface chemistry, and application of an external field.

Coupling of responsive materials with patterned surfaces at the micro/nanoscale often leads to interesting surface properties for potential applications, including dynamic colors,¹¹⁻¹³ reversible "gecko-like" adhesion,^{14,15} switchable hydrophilicity and hydrophobicity.¹⁶⁻¹⁸ Recently, many have begun to pattern micro-structured LCE actuators.^{7,8,10} To achieve a large and reversible strain, it is critically important to control LC anchoring within a patterned network at the molecular level. So far, in literature, the most common techniques to control LC anchoring are to rub the substrate and to apply a magnetic field before the LC monomers are cross-linked. Rubbing is effective when preparing non-patterned LCE membranes where LC molecules align along microgrooves generated by rubbing.^{6,19,20} However, rubbing often fails in the fabrication of micro- and nanostructures, for example, LCE micropillar arrays, not to mention the generation of static charge, scratches and potential high production cost of this technique.

Keller *et al.* first demonstrated the fabrication and actuation of NLCE micropillar arrays using a polydimethylsiloxane (PDMS) mold with cylindrical pores and by applying a magnetic field (1-1.5Tesla) to align LCs vertically along the film thickness in the mold.^{21,22} As a result, a large contraction strain (35%) was generated when actuating the pillars above T_{NI} (120°C) for side-chain NLCE micropillars.²² Nevertheless, detailed investigation (both experimentally and theoretically) of LC anchoring in such pillars remains lacking. In part, this is due to the fact that micro-patterned PDMS molds provide much more complicated topographical interfaces compared to a flat substrate, making it more challenging to control the LC anchoring. Given the wide range of potential applications of structured NLCEs, it is pressing to understand and eventually precisely control LC anchoring under confinement of PDMS molds during soft lithography, through surface topography, surface chemistry, and/or use of an external field.

Here, using a NLCE pillar array as a model system, we demonstrate the importance of surface chemistry in controlling LC alignment within micron-sized PDMS molds, and thus reversible actuation of NLCEs. Landau-de Gennes numerical modeling was performed to simulate the LC alignment in both homeotropic (i.e., vertical alignment) and planar anchoring of PDMS molds. We found that perfect alignment of NLC molecules along the pillar thickness can only be achieved in PDMS molds with planar anchoring surface chemistry, as opposed to the application of a strong magnetic field $(4.0 \times 10^5 \text{ A/m})$ in the vertical direction. Experimentally, we coated a thin layer of poly(2-hydroxyethyl methacrylate) (PHEMA) to the PDMS mold surface to create a degenerate planar surface for NLC small molecule, 4-Cyano-4'-pentylbiphenyl (5CB), and NLC monomer, (4"-acryloyloxybutyl)-2,5-di- (4'-butyloxybenzoyloxy) benzoate (LCM4), leading to full vertical alignment of NLCs inside the pores as confirmed by polarized optical microscope (POM). In comparison, NLCs in untreated PDMS mold maintained homeotropic anchoring at the interfaces and the director escaped from the center of the mold. The NLCE pillars with planar anchoring demonstrated a relatively large radial strain (\sim 30%) when heating across T_{NI}.

4.2 Experimental methods

4.2.1 Materials

(4"-acryloyloxybutyl)-2,5-di-(4'-butyloxybenzoyloxy)benzoate (LCM4) was synthesized according to the literature.³ N,N-dimethyl-n-octadecyl-3-amino-propyltrimethoxysilyl

chloride (DMOAP), hydroxyethyl methacrylate (HEMA), 1,6-hexane-diol diacrylate and 4-Cyano-4'-pentylbiphenyl (5CB) were purchased from Sigma Aldrich and used as received. Photoinitiator, Irgacure®184 (1-hydroxy cyclohexyl phenyl ketone), was obtained from Ciba Specialty Chemicals.

4.2.2 Preparation of PDMS molds

The PDMS porous membrane (diameter $10\mu m$, pitch $20\mu m$, and depth $40\mu m$) was replicated from the epoxy (D.E.R. 354, Dow Chemical) pillar master, following the protocol reported earlier.²³

4.2.3 Preparation of PDMS molds with different surface chemistry

The surface of as-cured PDMS porous membranes offered homeotropic anchoring to LCs for control experiments. To prepare a planar anchoring mold, a PDMS mold was immersed into a solution consisting of photo-initiator (Irgacure®184, 30 wt%) in acetone for 30 min, followed by rinsing with acetone three times and drying by air gun. The dried PDMS mold was immersed into neat HEMA liquid and exposed under UV light (365 nm, Hg lamp) at a dosage of 1000 mJ/cm². The resulting mold was rinsed by ethanol three times to remove unreacted HEMA monomers, followed by drying on a hot stage at 95°C.

4.2.4 Preparation of DMOAP coated glass substrates

1 vol% DMOAP solution was prepared in water. Then the glass slides were immersed into the solution for 30min, followed by washing with DI water for three times and baking at 110°C in an oven for 1 h.

4.2.5 Preparation of 5CB in the PDMS mold

A glass slide was pre-cleaned by washing with ethanol and acetone twice, respectively. Then one drop of 5CB (\sim 5µL) was placed on the glass slide, and the PDMS mold (untreated or treated) was applied on top. After filling the mold with 5CB by capillary force for 1 min, it was lifted and bladed with a razor blade on the top surface to remove the residual 5CB. A DMOAP treated glass slide was placed on top of the PDMS mold, and the sample filled with 5CB in the mold was characterized by polarized optical microscopy (POM).

4.2.6 Fabrication of LCM4 pillars

LCM4 and 1,6-hexanediol diacrylate were first mixed at a molar ratio of 4:1 in dichloromethane (20 wt%) to obtain a homogeneous solution, followed by addition of 2wt% of photoinitiator (Irgacure® 184). 20 μ L of the mixture was drop-cast on a clean glass slide and dried under vacuum. The mixture was then heated to 110°C on a hot stage and covered by the PDMS mold for 10 min. After the pores of the mold were completely filled with LCs, the glass slide was carefully removed, and a razor blade was used to scrape off the residual LCs. The PDMS mold was then placed on a DMOAP treated glass substrate, and the sample was examined under POM to check LC anchoring before UV exposure. The PDMS mold along with LC monomers was exposed to 365 nm UV light (97435 Oriel Flood Exposure Source from Newport, intensity of 54 mW/cm²) at 17,000 mJ/cm² dosage, followed by removal of the DMOAP coated glass substrate. The sample was then placed on top of a thin layer of polyurethane (PUA) liquid (Minuta Technology) on a clean glass slide, and exposed with another 17,000 mJ/cm² dosage of UV light to

bond PUA onto pillars. After the sample was cooled to room temperature, the PDMS mold was peeled off to obtain the LCE pillars supported on a PUA thin film.

4.2.7 Polarized optical microscopy

The liquid crystal structure was observed by an Olympus BX61 motorized optical microscope with crossed polarizers using CellSens software.

4.2.8 Landau-de Gennes numerical modeling

Numerical modeling of LC alignment within the PDMS mold was performed according to literature. The Frank elastic constants of 5CB at 298K,²⁴ $K_1 = 0.64 \times 10^{-11}$ N (splay), $K_2 = 0.3 \times 10^{-11}$ N (twist), and $K_3 = 1 \times 10^{-11}$ N (bend), were used. The simulation box to model 5CB in cylindrical pores was set as diameter 352 nm and height 1408 nm, that is, the aspect ratio (height/diameter) = 4, same as that of the micropillars in experiments. To evaluate the effect of vertical magnetic field on the alignment of LC molecules in the cylindrical pores, an external magnetic field *H* was applied in the simulation, which

contributed to the free energy as

$$f_{mag} = -\frac{1}{2}\mu_0 H_i \left(\chi \delta_{ij} + \Delta \chi Q_{ij}\right) H_j \tag{4-1}$$

where $\mu_0 \approx 1.2566 \times 10^{-6} N/A^2$ is the magnetic permeability of vacuum, *H* is the magnetic field strength, and χ and $\Delta \chi$ are the isotropic and anisotropic part of the magnetic susceptibility, respectively. Typically, for nematic LCs²⁵, χ and $\Delta \chi$ are positive with values on the order of 10⁻⁷. *H* was estimated from the magnetic flux density *B* by neglecting the magnetization *M* of 5CB in the external magnetic field.
$$H = \frac{B}{\mu_0} - M = \frac{B}{\mu_0} - \chi H$$
(4-2)

Therefore

$$(1+\chi)H = \frac{B}{\mu_0} \tag{4-3}$$

Since $\chi \ll 1$, $H \approx \frac{B}{\mu_0} = \frac{0.5 \text{ T}}{1.2566 \times 10^{-6} N/A^2} \approx 4.0 \times 10^5 \text{ A/m}.$

Here, the surface magnetic flux density B of the magnetic disk, used in literature^[9] with 1.5 Tesla demagnification flux density or magnetic flux density inside the magnet, was estimated at 0.5 Tesla. Flux density on the centerline of a rectangular magnet at a distance z from the magnet surface in the north-south pole direction can be calculated as

$$\boldsymbol{B} = \frac{B_r}{\pi} \left[\arctan\left(\frac{LW}{2z\sqrt{4z^2 + L^2 + W^2}}\right) - \arctan\left(\frac{LW}{2(D+z)\sqrt{4(D+z)^2 + L^2 + W^2}}\right) \right]$$
(4-4)

where B_r is the magnet flux density inside the magnet, z is the distance from the magnet surface, and L, W, D are the length, width, thickness of the rectangular magnet, respectively. Therefore, from Eq. (4) we can calculate B at z = 0.01 mm above the magnet with L = 30 mm, W = 20 mm, D = 10 mm and $B_r = 1.5$ T, to be around 0.45 T. For a cylinder (or disc) magnet, B can also be estimated in a similar manner. As shown in Eq. 4, the flux density B decays rapidly with increasing z. However, decay of magnetic field through the sample was neglected in this simulation.

4.3 Landau-de Gennes numerical modeling

So far, fabrication of LCE microstructures by soft lithography has focused on using an external field (e.g. magnetic field) to align LCs using non-treated PDMS molds.^{7,22,26} The freshly prepared PDMS surface has a low surface energy ($\sim 20 \text{ mJ/m}^2$). The commonly used small molecule nematic liquid crystal (NLC), 5CB, has weak homeotropic anchoring on PDMS surfaces. To understand the effect of surface chemistry vs. magnetic field to align NLCs, we first simulated the anchoring of 5CB in a PDMS porous membrane using Landau-de Gennes numerical modeling. As seen in Figure 4.1, 5CB filled in the untreated hydrophobic PDMS mold were barely aligned by the magnetic field (up to 0.5 Tesla) (Figure 4.1a). 5CB remained homeotropically anchored on the PDMS mold surface with or without the strong magnetic field, and the director of the LCs escapes from the center of the mold. Under this LC anchoring configuration, it is therefore challenging to achieve large actuation strain near T_{NI}, as molecular reorientation near the transition temperature would partially cancel with each other. Interestingly, when 5CB had planar anchoring within the PDMS mold, we observed that 5CB molecules were not only aligned along the LC/mold interface, but vertically oriented in the pores (Figure 4.1b). Such mono-domain alignment of the LCs within the mold could lead to a relatively large strain of the LCE pillars, which is necessary for actuation. Since no magnets will be needed to align the LC during sample preparation, the experimental set-up could be much simplified by controlling the interfacial chemistry.



Figure 4.1 Landau-de Gennes numerical modeling of 5CBs in a PDMS mold with (a) homeotropic anchoring and (b) planar anchoring with and without a magnetic field.

4.4 Control of liquid crystal surface anchoring

Guided by simulation results, we grafted a thin layer of PHEMA on the PDMS mold to introduce planar anchoring of LCs (**Figure 4.2a**). While planar anchoring of LCs on a glass slide is usually achieved by absorbing a thin layer of poly(vinylalcohol) (PVA) or polyimide (PI) on the substrate, it is challenging to uniformly coat hydrophilic polymers, *i.e.* PVA or PI, on a hydrophobic PDMS mold. Here, we first treated the mold with the acetone solution of photoinitiator (Irgacure®184), which was expected to be partially trapped within the mold surface since PDMS could be slightly swollen by

acetone (swelling ratio ~1.03). The PDMS mold was then immersed into HEMA monomers, which wet the PDMS surface, followed by UV curing at different dosages to ensure complete coverage of PHEMA on the PDMS mold



Figure 4.2 (a) Schematic illustrations of the preparation of the PDMS molds with different surface chemistry and the fabrication of LCE pillar array. Pillar dimensions: diameter $10\mu m$, pitch (center-to-center distance) $20\mu m$ and height $40\mu m$. (b) Chemical structures of LC systems used in the experiments.

To ensure the complete coverage of PHEMA on PDMS mold, we monitored the water contact angles of the treated molds prepared at different UV dosages (**Figure 4.3**). At low UV dosages ($\leq 800 \text{ mJ/cm}^2$), the water contact angle of the mold was found greater than 50°. At 1000 mJ/cm², the lowest water contact angle (~27°) was achieved, suggesting sufficient coverage and polymerization of PHEMA. At a higher dosage (1500

mJ/cm²), the water contact angle increased again, possibly due to the increased thickness of the PHEMA layer, leading to larger roughness and a more hydrophobic surface.



Figure 4.3 Average water contact angles on PHEMA coated PDMS exposed to different UV dosages.

The cured PHEMA has very similar chemistry to PVA as they both have one hydroxyl group in each repeat unit. As evident from **Figure 4.4**, 5CB molecules and LCM4 monomers had planar anchoring in porous mold made of pure PHEMA, where the directors were nearly all vertically aligned.



Figure 4.4 POM images of 5CB (a) and LCM4 (b) in a PHEMA porous mold with pore diameter $10\mu m$, pitch $15\mu m$, and depth $20\mu m$. Vertical alignments of LC molecules were observed in both LC systems. Scale bar: $20\mu m$.

Anchoring of 5CB and LCE monomers (LCM4) in PDMS molds was further investigated under POM. For homeotropically anchoring molds, an escaped radial configuration is expected, as shown in **Figure 4.5a**. On the untreated PDMS mold, 5CB exhibited uniform escaping configuration (**Figure 4.5b**), while polydomain anchoring of LCM4 was observed with non-uniform light transmittance under POM (**Figure 4.5c**). In agreement with the simulation (**Figure 4.1**), alignment of 5CB in the PDMS mold were experimentally confirmed, including the escaping configuration in the homeotropic mold and vertical alignment in the planar mold. From **Figure 4.1**, simulation shows in both anchoring configurations, the director fields exhibit axial symmetry along the vertical axis, thus we discuss the topologies in the 2D manner of each radial slice of the nematics (**Figure 4.5a** and **d**). In homeotropic anchoring conditions, as illustrated in **Figure 4.5a**, alignment of 5CB created two sets of topological defects at the top corner and the bottom corner of the mold, respectively. Under constraint of the elastic energy, the director of LCs would escape from the center (dotted line), leading to a black dot under POM (red circle in **Figure 4.5b** inset), when the sample was viewed in the normal direction.



Figure 4.5 (a) Schematic of LC anchoring in a homeotropic anchoring mold. Red dotted line indicates the escaping direction of LC director. (b-c) POM images of (b) 5CB and (c) LCM4 in a homeotropic anchoring PDMS mold. Insert: LC escaping direction (red circle) under cross polarizers when observing the sample vertically. (d) Schematic of 5CB in a planar anchoring PDMS mold. (e-f) POM images of (e) 5CB and (f) LCM4 in a planar anchoring PDMS mold.

For planar anchoring, 5CB molecules were mostly vertically aligned with the topological defects appearing at the bottom of the mold, and no defect was found at the top corner (**Figure 4.5d**). Thus, under POM, most of the image was dark with only slightly bright dots coming from transmitting light through the bottom of the mold (**Figure 4.5e**). Interestingly, we found the anchoring behaviors of LCM4 in both untreated and treated PDMS molds were very similar to that of 5CB, despite the difference between the chemical structures of 5CB and LCM4. Even though LCM4 in the

homeotropic-anchoring mold exhibited polydomain alignment, escaping configuration samples have been achieved by applying a vertical magnetic field from a 1.5T permanent magnet⁷. In the planar anchoring mold, however, we found for the first time that POM images of LCM4 and 5CB (**Figure 4.5e-f**) were nearly identical, both of which showed slightly bright dots in the dark background. This indicated that LCM4 had molecular alignment in agreement with that of 5CB, which undoubtedly confirmed the vertical alignment of LCM4 molecules within the mold.

4.5 Actuation of cross-linked LCEs

After LCM4 was carefully cross-linked within the mold with planar anchoring, mono-domain alignment of LCM4 within the pillars was maintained as observed by POM; defects could be found on top of the pillars by comparing POM images of the pillars at 45° and 0° polarization angles (**Figure 4.6a-b**). Landau-de Gennes numerical modeling was employed to better understand the anchoring of the LCM4 and how these defects are formed when LCM4 infiltrates the PDMS mold (**Figure 4.6**). The observed defects arose from the planar anchoring of the monomer to the PDMS mold at the bottom of each micro-hole. As the planar anchoring strength was increased, the size of the defect domain is increased. In addition to the twist region, a defect ring was observed at the bottom of each micro-hole, which arose from the corner energy (**Figure 4.7**). From the calculations, we estimated the planar anchoring strength to be on the order of 1-10 J/m² and corner energy to be about ten times smaller than the anchoring strength.



Figure 4.6 Landau-de Gennes numerical modeling of 5CBs in a PDMS mold with planar anchoring strength of (a) 0.1, (b) 1, and (c) 10 J/m^2 without corner energy.



Figure 4.7 Landau-de Gennes numerical modeling of 5CBs in a PDMS mold with ratio of planar anchoring strength to corner energy of (a) 1:0.1, (b) 10:1, and (c) 10:0.1.

Across T_{NI} , this mono-domain vertical alignment of LC molecules led to a relatively large strain in the radial direction (~30%), measured from the diameters in the middle of the pillars at 50°C and 110°C, respectively (**Figure 4.6c-d**). Actuation of LCM4 pillars was also characterized through the top view of the sample under bright field (BF) microscopy, as shown in **Figure 4.6f**. A 30% radial strain could also be measured from **Figure 4.6f**. Upon heating above T_{NI} , a slightly titling of the pillars was found at 110°C, which can be explained by the instability of the pillars caused by the different thermal expansion coefficients between polyurethane (PUA) supporting layer and LCM4 pillars. Such tilting behavior can be recovered when the sample was cooled

down, but minor residual deformation remained. The measured strain value was consistent with literature for LCM4 nano-fibers (~300 nm in diameter, 6 µm in length) templated from anodic aluminum oxide (AAO) membrane with 20 mol% cross-linker²⁷. AAO surface also has a large amount of hydroxyl groups, thus, providing planar anchoring of LCM4. Although in the later case, AAO template has to be chemically etched to obtain the pillars, while here we can peel off the LCM4 pillars from the PDMS mold.



Figure 4.8 (a-b) Cross-sectional views of POM images of LCM4 pillars after UV curing at (a) 45° and (b) 0° angle between the polarizer and the nematic director.(c-d) Cross-sectional views of BF images of LCM4 pillars at 50°C (c) and 110°C (d). (f) Top-view BF image of LCM4 pillars at a heating and cooling cycle. Blue and Red arrows in (c-f) indicate the position of pillars for measurement of diameter at 50°C and 110°C, respectively. Length of arrow: blue-8.6 μ m, red-11.1 μ m. Scale bar: 20 μ m.

4.6 Conclusions

We demonstrated the importance of interfacial chemistry in molding LCE microstructures. Using Landau-de-Gennes numerical modeling, we showed that vertical alignment of LC monomers could only be achieved within PDMS mold when LCs had planar anchoring at the LC-mold interface and not in molds with homeotropic anchoring with or without an applied magnetic field. LC monomers in the mold with homeotropic anchoring surface, however, always exhibited an escaping configuration. By coating of PHEMA to the PDMS mold surface, we switched the mold surface from hydrophobic to hydrophilic, thus turning the LC anchoring from homeotropic to planar for both 5CB and LCM4, leading to highly uniform mono-domains of LC alignment along the film thickness. After cross-linking LCM4 monomers, the alignment of LCE pillars was maintained, leading to a large radial strain (30%) across T_{NI} compared to almost no change if the mold surface was not treated.

The concept of controlling interfacial chemistry in soft-lithography is much simpler and more effective than the use of an external field to direct LC anchoring over a large area, especially in the case of more complex systems, such as porous membranes, channels, and 3D structures. By combining topology and interfacial chemistry to manipulate the boundary conditions within the micro- and nanostructures, we expect to observe much richer library of LCE actuation behaviors. In turn, it could intrigue and facilitate the exploration of LC anchoring theory in LCEs for potential applications, including actuators, displays, sensors, dry adhesion, photonic materials, and "origami-like" folding of 2D structures into 3D.

4.7 Contributions

Xia, Y., **Lee, E.,** Hu, H., Gharbi, M. A., Beller, D.A., Fleischmann, E., Kamien, R. D., Zentel, R. and Yang, S. "Control of liquid crystal anchoring in liquid crystal elastomer pillar arrays by interfacial chemistry." Manuscript in preparation.

Xia, Y., Lee, E. and Hu, H performed the liquid crystal elastomer experiments and data

analysis. Xia, Y. performed simulation of LCM4 in pillars using the code developed by

Beller, D.A. and Kamien, R., D., who also provided theoretical insights. Gharbi, M. A.,

participated in discussion and provided physical insights of experiments. Fleischmann, E.

and R. D. Zentel provided initial LCM4 materials for testing the concept, while Xia, Y.

later synthesized large quantities of LCM4 to carry out the experiments reported here.

4.8 References

- 1 Warner, M. & Terentjev, E. M. *Liquid crystal elastomers*. Vol. 120 (Oxford University Press, 2003).
- Spillmann, C. M., Naciri, J., Chen, M.-S., Srinivasan, A. & Ratna, B. R. Tuning the physical properties of a nematic liquid crystal elastomer actuator. *Liq Cryst* 33, 373 doi:10.1080/02678290500494921 (2006).
- 3 Thomsen, D. L. *et al.* Liquid crystal elastomers with mechanical properties of a muscle. *Macromolecules* **34**, 5868, doi:10.1021/Ma001639q (2001).
- 4 Li, M.-H. & Keller, P. Artificial muscles based on liquid crystal elastomers. *Phil Trans R Soc A* **364**, 2763, doi:10.1098/rsta.2006.1853 (2006).
- 5 Jin, L. H., Lin, Y. & Huo, Y. Z. A large deflection light-induced bending model for liquid crystal elastomers under uniform or non-uniform illumination. *Int J Solids Struct* **48**, 3232, doi:10.1016/j.ijsolstr.2011.07.015 (2011).
- 6 Ohm, C., Brehmer, M. & Zentel, R. Liquid crystalline elastomers as actuators and sensors. *Advanced Materials* **22**, 3366, doi:10.1002/adma.200904059 (2010).

- 7 Cui, J. *et al.* Bioinspired actuated adhesive patterns of liquid crystalline elastomers. *Advanced Materials* **24**, 4601, doi:10.1002/adma.201200895 (2012).
- 8 Liu, D., Bastiaansen, C. W. M., den Toonder, J. M. J. & Broer, D. J. Photoswitchable surface topologies in chiral nematic coatings. *Angewandte Chemie International Edition* **51**, 892, doi:10.1002/anie.201105101 (2012).
- 9 Urayama, K., Honda, S. & Takigawa, T. Deformation coupled to director rotation in swollen nematic elastomers under electric fields. *Macromolecules* **39**, 1943, doi:10.1021/ma052762q (2006).
- 10 van Oosten, C. L., Bastiaansen, C. W. M. & Broer, D. J. Printed artificial cilia from liquid-crystal network actuators modularly driven by light. *Nature Materials* 8, 677, doi:10.1038/nmat2487 (2009).
- 11 Sato, O., Kubo, S. & Gu, Z.-Z. Structural color films with lotus effects, superhydrophilicity, and tunable stop-bands. *Accounts of Chemical Research* **42**, 1 (2008).
- 12 Kim, H. *et al.* Structural colour printing using a magnetically tunable and lithographically fixable photonic crystal. *Nature Photonics* **3**, 534, doi:10.1038/Nphoton.2009.141 (2009).
- 13 Ge, J., Hu, Y. & Yin, Y. Highly tunable superparamagnetic colloidal photonic crystals. *Angewandte Chemie* **119**, 7572, doi:10.1002/anie.200701992 (2007).
- 14 Kamperman, M., Kroner, E., del Campo, A., McMeeking, R. M. & Arzt, E. Functional adhesive surfaces with "gecko" effect: The concept of contact splitting. *Advanced Engineering Materials* **12**, 335, doi:10.1002/adem.201000104 (2010).
- 15 Glassmaker, N. J., Himeno, T., Hui, C.-Y. & Kim, J. Design of biomimetic fibrillar interfaces: 1. Making contact. *Journal of The Royal Society Interface* **1**, 23, doi:10.1098/rsif.2004.0004 (2004).
- 16 Krupenkin, T. N., Taylor, J. A., Schneider, T. M. & Yang, S. From rolling ball to complete wetting: The dynamic tuning of liquids on nanostructured surfaces. *Langmuir* **20**, 3824, doi:10.1021/la036093q (2004).
- 17 Lin, P.-C. & Yang, S. Mechanically switchable wetting on wrinkled elastomers with dual-scale roughness. *Soft Matter* **5**, 1011, doi:10.1039/B814145B (2009).
- 18 Chen, C.-M. & Yang, S. Directed water shedding on high-aspect-ratio shape memory polymer micropillar arrays. *Advanced Materials* **26**, doi: 10.1002/adma.201304030, doi:10.1002/adma.201304030 (2013).
- 19 Woltman, S. J., Jay, G. D. & Crawford, G. P. Liquid-crystal materials find a new order in biomedical applications. *Nature Materials* **6**, 929, doi:10.1038/nmat2010 (2007).
- 20 Yu, Y. & Ikeda, T. Soft actuators based on liquid-crystalline elastomers. Angewandte Chemie International Edition **45**, 5416, doi:10.1002/anie.200601760 (2006).
- 21 Yang, H. *et al.* Micron-sized main-chain liquid crystalline elastomer actuators with ultralarge amplitude contractions. *Journal Of the American Chemical Society* **131**, 15000, doi:10.1021/ja905363f (2009).
- 22 Buguin, A., Li, M.-H., Silberzan, P., Ladoux, B. & Keller, P. Micro-actuators: When artificial muscles made of nematic liquid crystal elastomers meet soft

lithography. *Journal of the American Chemical Society* **128**, 1088, doi:10.1021/ja0575070 (2006).

- 23 Zhang, Y., Lo, C.-W., Taylor, J. A. & Yang, S. Replica molding of high-aspectratio polymeric nanopillar arrays with high fidelity. *Langmuir* 22, 8595, doi:10.1021/la061372+ (2006).
- 24 Kleman, M. & Laverntovich, O. D. Soft matter physics: An introduction. (Springer, 2003).
- 25 Stark, H. Physics of colloidal dispersions in nematic liquid crystals. *Physics Reports* **351**, 387, doi:10.1016/S0370-1573(00)00144-7 (2001).
- 26 Wei, R. B., Zho, L. Y., He, Y. N., Wang, X. G. & Keller, P. Effect of molecular parameters on thermomechanical behavior of side-on nematic liquid crystal elastomers. *Polymer* **54**, 5321, doi:10.1016/j.polymer.2013.07.057 (2013).
- 27 Ohm, C., Haberkorn, N., Theato, P. & Zentel, R. Template-based fabrication of nanometer-scaled actuators from liquid-crystalline elastomers. *Small* **7**, 194, doi:10.1002/smll.201001315 (2011).

CHAPTER 5: Self assembly and actuation of gold nanorods in liquid

crystal over micropillar arrays for tunable plasmon resonance

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5.1 Introduction

Control over the assembly of functional, nanostructured materials is imperative for the realization of novel nanodevices. Much work has focused on the assembly of metal-nanoparticles due to their applications in energy harvesting,¹ sensing,² metamaterials,³ and catalysis.⁴ Gold nanorods (AuNRs), in particular, have received considerable interest due to the facile synthesis of variable size and aspect ratios,^{5,6} diverse chemistry for surface modification,⁷⁻¹¹ and anisotropic optical properties.¹² Collective oscillations of free electrons at the surface of metal nanoparticle surfaces interact with light to cause strong resonances in the optical region of the electromagnetic spectrum, known as localized surface plasmon resonance (LSPR). Owing to their shape, AuNRs have two such absorbance bands, a transverse mode and a longitudinal mode, which depend on the diameter and length of the AuNR, respectively. Furthermore, AuNRs have significantly enhanced electric fields near their tips, which make AuNRs attractive for use as a sensing platform based on surface enhanced Raman spectroscopy (SERS).^{13,14} However, in order to apply them for any optical device, it is essential to control the assemblies of AuNRs, and thus their optical properties.

The absorbance of AuNRs significantly changes when AuNRs come into close contact with each other due to plasmonic coupling. For instance, when two AuNRs come together side-by-side the absorbance band undergoes a hypsochromic (blue) shift, whereas when two AuNRs come together end-to-end the absorbance band undergoes a bathochromic (red) shift.¹² The strength of the shift depends upon the number of AuNRs in the assembly and their spacing. AuNRs can be assembled in solutions in a controlled manner.⁹⁻¹¹ However, solution assembly may not be desired in device fabrication. More recent work has shown controlled assemblies of AuNRs in polymer matrices,^{8,15} but the optical properties cannot be tuned once the films are cast. Therefore, a more dynamic approach, where AuNRs can be reversibly assembled and disassembled triggered by a specific stimulus, is attractive to realize the full potentials of AuNR-based nanodevices.

Liquid crystal (LC), an anisotropic soft matter introduced in Chapter 1.3.4, is one such promising candidate for the reversible tuning of the assemblies of AuNRs. The alignment of LCs can be controlled by surface chemistry, surface topography, or by external field. The coupling of the optical properties of AuNRs with the spontaneous order-disorder transitions of LCs upon triggering by external stimuli such as heat, light and electrical field will offer great capabilities for active plasmonic devices. This coupling can be achieved in several ways, including functionalizing AuNRs with liquid crystalline ligands, depositing an active LC layer over immobilized AuNRs, and simply mixing AuNRs with LCs. Umadevi *et al.* showed that AuNRs functionalized with a liquid crystalline ligand could be assembled into large scale aggregates with some ordering.¹⁶ However, further manipulation and dynamic tuning of the optical properties was not shown. Several groups have shown that the optical properties of metallic particle

arrays could be tuned by assembling LCs on top of them.¹⁷⁻²¹ However, only a small shift of plasmon resonance peak (<50 nm) and a drop in peak intensity were observed upon application of an electric field. It is suggested that the change in optical properties is the result of change in the refractive index of the LC medium due, via changing the alignment of the LC molecules, rather than by the actuation of the active plasmonic particles. Liu *et al.* showed AuNRs could be directionally aligned in the nematic phase of a LC, leading to polarization-dependent optical properties of the AuNR/LC dispersion.^{22,23} However, the unique temperature-dependent properties of LCs were not further exploited to actuate the AuNRs. While these previous studies have shown the coassembly of AuNRs and LCs, none have demonstrated direct manipulation of the optical responses of AuNRs by LC phase transitions.

Recent theoretical²⁴ and experimental²⁵ work has demonstrated the sequestration of individual AuNRs into the defects in ordered LC phases. However, the reversible clustering of nanoparticle ensembles to tune the plasmonic resonance has not been realized. In this work, we exploit the anisotropic thermal, optical and elastic properties of LCs to tune the clustering of AuNRs, and thereby modulating their plasmonic resonances. By exploiting the confinement of smectic-A LCs (SmA LCs) to topographically patterned pillars, we show that defects can be formed at precise locations around each pillar and tuned by varying the temperature of the system. When dispersing polystyrene (PS)functionalized AuNRs into the LC prior to drop-casting onto the polymer pillar arrays, the AuNRs are spontaneously assembled into the defects surrounding pillars. The dimensions of the defect structure and consequently, the nanorod assembly can be altered by heating and cooling. Accordingly, the plasmonic peaks shift with temperature. By optimizing the surface anchoring conditions (homeotropic vs. planar) and aspect ratio (AR = height/diameter) of the pillar arrays, we can maximize the plasmonic peak shift. For homeotropic anchoring epoxy pillars with an AR= 1.3, the transverse and longitudinal local surface plasmonic peak shift are ~100 and ~150 nm, respectively.

5.2 Experimental methods

5.2.1 Surface functionalization of gold nanorods with polystyrene

Three 40 mL solutions of cetyltrimethylammonium bromide (CTAB) coated AuNRs in deionized (DI) water were synthesized by a seed-mediated growth method as outlined elsewhere.⁵⁻⁷ Excess CTAB was removed through two washing cycles consisting of centrifugation (20 min at 8,000 RPM, Eppendorf 5804) followed by replacement of the supernatant with approximately 40 mL of Milli-Q water. Following the washing steps, the three AuNR solutions were combined and concentrated in 40 mL of water, providing a stock solution of concentrated AuNRs.

The stock solution of AuNRs (9 mL, 0.4 nM) in DI water was centrifuged (20 min at 8,500 RPM, Eppendorf 5804) and the supernatant was removed so that there was only a small aliquot of concentrated AuNR solution. 30 mg of 5,300 g/mol thiol-terminated polystyrene (HSPS) (Polymer Source) was added to a solution of 10 mL THF until dissolved. Next, the AuNR aliquot was added to the THF/HSPS solution under stirring. The solution was stirred overnight and then solvent exchanged to chloroform twice to remove free HSPS. Finally, AuNRs were suspended in 1 mL of chloroform.

5.2.2 Substrate functionalization

To achieve planar anchoring, the epoxy pillars or glass cover slips were treated with UVO (Jelight, model 144AX) for 1 h and used immediately. For homeotropic anchoring substrates, silicon tetrachloride was evaporated onto the epoxy pillars or glass cover slips in a vacuum dessicator for 10 min.²⁶ Then, the substrates were placed into a 65°C oven with water vapor for 10 min, forming a silica thin film. The substrates were then immersed 3 into wt% ethanol solution of dimethyloctadecyl[3а (trimethoxysilyl)propyl]ammonium chloride (DMOAP) for 1 h. They were then washed with DI water 3 times and dried in a 100°C oven.

5.2.3 Assembly of gold nanorods in liquid crystals

4'-n-octyl-4-cyano-biphenyl (8CB) (Sigma Aldrich or Kingston Chemicals) was added to the chloroform solution of PS-AuNR and ultra-sonicated for dispersion. The chloroform was then evaporated using a vacuum oven at room temperature. The suspension was heated to 45°C (above the nematic-isotropic transition temperature, T_{NI}) and drop cast over the surface-treated epoxy pillars. A surface-treated glass cover slip was used to close the liquid crystal cell.

5.2.4 Characterization

Transmittance of the AuNR and PS-AuNR suspensions as synthesized were measured using the Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies). The LC cell was mounted on a Mettler FP82 hot stage equipped with FP 90 controller and heated at 45° C for 5 min to reach the isotropic group. It is then cooled down to 25° C at a rate of 10° C min⁻¹ to form the smectic-A (SmA) phase. In parallel to the heating and cooling

cycle, the LC textures were observed under the Olympus BX61 motorized optical microscope with crossed polarizers using CellSens software. Alternatively, the transmission of the LC cell is measured using a custom-built spectrophotometer with a fiber-coupled tungsten-halogen light source and a USB4000 detector (Ocean Optics).

5.3 Optical properties of gold nanorods

The functionalization of the AuNRs with PS is detailed in **Figure 5.1a**. Assynthesized PS-AuNRs displayed two characteristic extinction bands at 512 nm (transverse band) and 727 nm (longitudinal band) in water, as can be seen in **Figure 5.1b**. The longitudinal band underwent a slight bathochromic (red) shift to 742 nm after AuNRs are functionalized with HSPS and solvent exchanged to chloroform, as seen in **Figure 5.1c**. Finally, PS-AuNRs were characterized via SEM (**Figure 5.1d**) with length of 31 ± 4 nm and diameter of 11.3 ± 1.5 nm.



Figure 5.1 (a) Schematic detailing the functionalization of AuNRs with polystyrene brushes. (b-c) Extinction spectra of (b) AuNRs in water and (b) PS-AuNRs in chloroform. (d) SEM image of PS-AuNRs.

5.4 Control of liquid crystal surface anchoring

Square arrays of cylindrical epoxy micropillars (diameter = 10 μ m, pitch = 20 μ m) with various aspect ratios (=height/diameter 0.9, 1.3, and 1.6) were prepared by replica molding followed by surface functionalization to introduce different surface anchoring properties (**Figure 5.2a**). Homeotropic or planar anchoring was imposed on the surfaces of the pillars as well as the glass cover slip. PS-AuNRs dispersed in smectic-A LC, 4'-n-octyl-4-cyano-biphenyl (8CB), were sandwiched between the pillars and a glass cover slip to form a LC cell. The structure and phase transition temperatures of 8CB

are shown in **Figure 5.2b**. The cell was heated above the clearing temperature to the isotropic phase and subsequently cooled to the nematic phase.



Figure 5.2 Schematic of the substrate functionalization.

When the homeotropic boundary conditions were imposed on the pillars and cover slip, distortions to the director field appeared in the form of bright lines encircling the micropillars when observed under crossed polarizers (**Figure 5.3**). Outside these bright lines, the entire region was dark even under sample rotation, due to complete homeotropic anchoring on all surfaces.



Figure 5.3 Polarized optical microscopy images of PS-AuNRs in 8CB with homeotropic anchoring epoxy pillar arrays and cover slips. Pillar dimensions are diameter = 10 μ m, spacing = 10 μ m, and AR = 0.9 (a-b), 1.3 (c-d), and 1.6 (e-f). The temperature is 35°C (nematic, a, c, e) and 30°C (smectic, b, d, f). Scale bars: 20 μ m.

There should be three possible LC director field configurations within the pillar arrays with homeotropic anchoring, including uniform escaping of the director field and bulk disclination lines with either $\pm 1/2$ or $\pm 1/2$ winding geometry (**Figure 5.4**). The director fields exhibit axial symmetry along the vertical axis and can be discussed in terms of each radial slice of the nematic LCs. The director fields correspond to the local minima of the Landau-de Gennes free energy of a nematic LC surrounding a cylindrical micropillar sandwiched between two planar substrates, all with homeotropic anchoring, as previously reported.²⁷ At the top and bottom corners of the micropillar, the LC can have positive or negative winding via splay or bend elastic deformations, respectively. If there is opposite winding at the corners, then there exists uniform escaping of the director field. Bulk disclination lines with $\pm 1/2$ or $\pm 1/2$ winding numbers result from positive or negative winding at both corners, respectively.



Figure 5.4 Schematic of the director field lines of 8CB in the nematic phase between two pillars. (a) Uniform escaping of the director field and (b) bulk disclination lines with +1/2 and (c) -1/2 winding number. X indicates the defect location.

Image analysis was used to further investigate the circle dimensions for homeotropically-anchoring micropillars. The radius of the rings depended on the temperature and the aspect ratio of the pillars (**Figure 5.5**). For pillars with AR = 0.9 (**Figure 5.5a**), the average ring radius in the nematic range $33-38^{\circ}$ C was $8.8 \pm 0.2 \,\mu$ m

and the maximum ring radius was 9.1 μ m. There was no clear dependence of the ring radius on the temperature. For pillars with AR = 1.3 (**Figure 5.5b**), the average ring radius in the nematic range 33-38°C was 8.3 ± 0.8 μ m. The ring increased in size as the sample is cooled with the maximum ring radius 9.4 μ m at 33°C. For pillars with AR = 1.6 (**Figure 5.5c**), the average ring radius in the nematic range 33-38°C was 7.7 ± 0.2 μ m. The ring increased in size as the sample is cooled with the sample is cooled with the maximum ring radius in the nematic range 33-38°C was 7.7 ± 0.2 μ m. The ring increased in size as the sample is cooled with the maximum ring radius 8.1 μ m at 33°C. The changes in ring dimensions are summarized in **Figure 5.6**.



Figure 5.5 Polarized optical microscopy images of PS-AuNRs in 8CB with homeotropic anchoring epoxy pillar arrays and cover slips. Pillar dimensions are diameter = 10 μ m, spacing = 10 μ m, and AR = 0.9 (a), 1.3 (b), and 1.6 (c). The temperature (°C) is indicated in the bottom center of each image. Scale bars: 20 μ m.



Figure 5.6 Radius of the outer defect as a function of the temperature below the nematic-to-isotropic transition temperature.

As the sample was further cooled, 8CB transitioned into the smectic phase at \sim 32°C. Homeotropic anchoring can induce three possible LC structures in the smectic phase due to geometric frustration between uniform layer spacing, mean curvature, and Gaussian curvature imposed by the boundary conditions. For AR = 0.9, the structure of 8CB around a single micropillar appeared as a bright square octasect by intersecting dark lines under POM (**Figure 5.3b and 5.5a/32°C**). In 3D space, this should correspond to intersecting concentric cylindrical smectic layers wrapped around a lattice of intersecting line defects (**Figure 5.7a**), a smectic blue phase previously calculated by DiDonna *et al.*²⁸ The 2D projection of the proposed structure overlaid with the POM image (**Figure 5.7b**) shows good agreement. For AR = 1.3, 8CB appeared dark between nearest neighbor micropillars with Maltese cross patterns between next-nearest neighboring pillars under POM (**Figure 5.3d and 5.5b/32°C**). The dark regions represent smectic layers with

homeotropic alignment of the LCs, with both the layer normal and local director parallel to the surface normal of the substrate. Thus, the edges of the dark regions have planar anchoring perpendicular to the surface normal. The hybrid anchoring with planar at the sides and homeotropic at the top and bottom boundaries led to the formation of focal conic domains (FCDs), where the smectic layers are wrapped around two disclination lines formed by a circle and a straight line through the circle center (Figure 5.7c).²⁹ The boundaries of the FCDs are overlaid with the POM image (Figure 5.7d) for clarity. Finally, for AR = 1.6, 8CB appeared dark throughout the sample with slight brightness around the edge of the micropillars under POM (Figure 5.3f and 5.5c/32°C). In 3D, this should correspond to parallel smectic layers confined by homeotropic anchoring at all interfaces with defects at the side interfaces (Figure 5.7e). These defects may be high density dislocations created at the pillar edge due to meniscus formation during the nematic-to-smectic phase transition.³⁰ Here, the micropillars and the top and bottom surfaces form the boundaries with homeotropic anchoring (Figure 5.7f). The expressed configuration in the smectic phase clearly depended on the aspect ratio of the pillars and also indicates the director field configuration in the nematic phase. As the aspect ratio increases, less bending of the smectic layers was observed, resulting in uniform homeotropic anchoring. The intersecting concentric cylindrical smectic layers, FCDs, and parallel smectic layers corresponded to bulk disclination lines with +1/2 winding geometry, uniform escaping of the director field and bulk disclination lines with -1/2winding geometry in the nematic phase, respectively. We note that the exhibited textures could also depend on the cooling rate, which is not considered here.



Figure 5.7 Schematic of the proposed minimum energy surfaces of 8CB in the smectic phase between micropillars (a, c, e) overlaid with the corresponding POM images (b, d, f). Pillar dimensions are diameter = 10 μ m, spacing = 10 μ m, and AR = 0.9 (a-b), 1.3 (c-d), and 1.6 (e-f). (a) Surfaces constructed by intersecting concentric cylindrical smectic layers wrapped around a lattice of intersecting line defects. Reproduced with permission

from reference 28. (b) POM image overlaid with the top-down view of the intersecting cylinders and line defects. Red and green rectangles indicate cylinders. Black lines indicate the line defects. Blue lines indicate where the cylinders intersect, i.e. where the smectic layers bend. (c) An FCD formed by confining smectic layers within a cylinder of planar anchoring on the sides and homeotropic anchoring at the top and bottom surfaces. Copyrighted image from reference 29. (d) POM image overlaid with the top-down view of the confining cylinders (blue circles). Red dots indicate the disclination lines perpendicular to the viewing plane. (e) Parallel smectic layers confined by homeotropic anchoring at all interfaces with bending of the layers at the side interfaces. (f) POM image overlaid with red circles indicating the micropillars and a blue line indicating the cross-sectional view of the smectic layers shown in (e).

For comparison, LC cells with planar anchoring were also fabricated. The defects

of the planar cells were highly disordered in both the nematic and smectic phases (Figure

5.8).



Figure 5.8 Polarized optical microscopy images of PS-AuNRs in 8CB over planar anchoring epoxy pillar arrays. Pillar dimensions are diameter = $10 \mu m$, spacing = $10 \mu m$, and AR= 0.9 (a-b), 1.3 (c-d), and 1.6 (e-f). The temperature is 35°C (nematic, a, c, e) and 30°C (smectic, b, d, f). Scale bars: $20 \mu m$.

5.5 **Optical response**

The transmission of PS-AuNRs in 8CB between micropillars with AR = 1.3 with homeotropic anchoring was measured as the sample was cooled from the isotropic phase. The spectra were normalized and subtracted from 1 to calculate extinction and offset for visualization (Figure 5.9a). At 40°C, 8CB was in the isotropic phase and the rods were uniformly distributed within the LCs and a peak could be observed at about 636 nm. At 38°C, 8CB has transitioned into the nematic phase and the peak red shifted to about 683 nm. At 36°C, two peaks could be observed at about 414 nm and 712 nm, corresponding to the transverse LSPR (TLSPR) and longitudinal LSPR (LLSPR), respectively. As the sample was further cooled through the nematic phase to 33° C, the TLSPR red shifted to 453 nm and the LLSPR red shifted to 729 nm. As the sample transitions to the smectic phase at 32°C, the plasmon peaks further red shifted to 483 nm and 789 nm but minimal shift was observed as the sample was cooled through the smectic phase to room temperature. The total peak shift for the TLSPR and LLSPR were 101 and 153 nm, respectively. This shift was one order of magnitude higher than that of systems previously reported based on the refractive index change of LC over metal nanoparticle arrays deposited on a surface.¹⁷⁻¹⁹ The plasmonic peak shift observed came from the dynamic interaction of the PS-AuNRs and the highly ordered LC defect ring structures. The change in the peak could be correlated to the defect ring radius (**Figure 5.9b**). As the sample was cooled, the ring radius increased, resulting in the compression of the LC director field and a red shift of the plasmon peak. The peak shift was reversed upon heating the sample.



Figure 5.9 (a) Extinction spectra of PS-AuNRs in 8CB over homeotropic epoxy pillars. The extinction is offset for clarity. Red, blue, and black colors indicate isotropic, nematic, and smectic phase, respectively. (b) The defect radius of the LC and transverse localized surface plasmonic resonance wavelength of the PS-AuNRs over epoxy pillars as a function of temperature.

For comparison, the transmission of the PS-AuNRs in 8CB in a planar LC cell was measured at various temperatures (**Figure 5.10a**). At 40°C, 8CB was in the isotropic phase and slight distinction peaks were observed at ~516 and 887 nm, which might be attributed to the TLSPR and LLSPR of the PS-AuNRs, respectively. As the cell was cooled to the nematic phase, the same peaks were observed. Due to the disordered defect structure of the planar cell, the peaks were insignificant. PS-AuNRs were randomly dispersed within the LC structure. In addition, they may have aggregated during the isotropic-nematic phase transition due to capillarity. In the smectic phase, peaks with

slightly higher intensity could be observed at the same positions. This may be due to the higher order of the smectic phase. No plasmon peaks shifts were observed for PS-AuNRs dispersed between planar anchoring micropillars upon cooling, in sharp contrast to the large shifts observed for the homeotropic anchoring micropillars (**Figure 5.10b**). Therefore, it was imperative to control the anchoring conditions of the micropillar arrays to direct the assembly and optical response of PS-AuNRs in the LC defect structures.



Figure 5.10 (a) Extinction spectra of PS-AuNRs in 8CB over planar epoxy pillars. The extinction is offset for clarity. Red, blue, and black colors indicate isotropic, nematic, and smectic phase, respectively. (b) The transverse and longitudinal localized surface plasmonic resonance peak position as a function of temperature for both homeotropic and planar cells.

To further demonstrate the importance of the micropillar array in assembling the AuNRs, a LC cell consisting of two flat glass slides treated with homeotropic anchoring on top and bottom was fabricated. As seen in **Figure 5.11**, no plasmon peaks were observed. In POM images, aggregation of the rods was observed when cooling the sample from the isotropic phase to the nematic phase transition, which could be attributed to capillarity (**Figure 5.11b-e**).



Figure 5.11 (a) Extinction spectra of PS-AuNRs in 8CB sandwiched between two glass slides with homeotropic anchoring. The extinction is offset for clarity. Red, blue, and black colors indicate isotropic, nematic, and smectic phase, respectively. (b-e) POM images of PS-AuNRs in 8CB in a homeotropic flat cell; the sample is transitioning from the nematic to the smectic phase from b to e.

As mentioned earlier, the appearance of 8CB smectic phases was highly dependent on the aspect ratio of micropillar arrays. Therefore, we expected the optical properties of AuNRs dispersed in 8CB over micropillar arrays would be dependent on AR too. As seen in Figure 5.12, for micropillars with AR = 0.9, two peaks were observed: the LLSPR shifting from 431 nm to 593 nm and the TLSPR shifting from 464 nm to outside the detector range into the UV region when cooled from 40°C to 28°C

(Figure 5.12a). The total peak shift for the observed LLSPR was 165 nm. No peaks were observed for micropillars with AR = 1.6 (Figure 5.12b). We correlated the peak shift to the observed ring defect size. As seen in Table 5.1, pillars with AR = 0.9 and 1.3 both had larger ring radii on the order of the pillar spacing. However, for AR=1.6, the ring radius was smaller and so the defect rings were not compressed against each other, therefore, there was no measureable peak shift. In addition, for AR=0.9, the change in ring radius as the temperature is swept was much smaller than that of AR=1.3. However, it shows a comparable resonance peak shift; this may indicate that the ring size change does not matter as much as the largest ring size, which allowed for the interaction of the defect structures from pillar to pillar (Figure 5.12c). Our hypothesis is that the large ring radius induced a compression of the LC director field, allowing for the coupling of the surface plasmon resonance of the PS-AuNRs.



Figure 5.12 Extinction spectrum of PS-AuNRs in 8CB over homeotropic epoxy pillars, with diameter = $10 \ \mu\text{m}$, spacing = $10 \ \mu\text{m}$ and AR = 0.9 (a) and 1.6 (b). Red, blue, and black colors indicate isotropic, nematic, and smectic phase, respectively. (c) The
transverse and longitudinal localized surface plasmonic resonance peak position as a function of temperature for epoxy pillars with AR = 1.3 and AR = 0.9.

Table 5.1 Comparison of the defect ring sizes and the plasmon peak shift of PS-AuNRsin 8CB over homeotropic pillar arrays of different aspect ratios.

Pillar Aspect Ratio	0.9	1.3	1.6
Outermost Ring Radius Max (µm)	9.1	9.4	8.1
Outermost Ring Radius Min (µm)	8.6	7.4	6.9
Change in Ring Radius (µm)	0.5	2.0	1.2
Peak Shift (nm)	165.3	173.2	N/A

Besides the aspect ratio effect, we wondered whether the anisotropy of LCs (e.g. polarization sensitivity) plays a role or not. Since AR = 1.3 gave the largest peak shift, we investigated the polarization dependence of the transmission of PS-AuNRs in 8CB within pillars with AR = 1.3 and homeotropic anchoring was measured (**Figure 5.13**). The polarization angle was fixed and the transmission spectrum was measured every 1°C as the sample was cooled from 40°C to 31°C. The polarizer was then rotated by 30° and the measurements were then repeated. As seen in **Figure 5.13**, no polarization dependence was observed, possibly because the micropillars have circular cross-sectional shapes.



Figure 5.13 (a) The peak resonance wavelength as a function of polarization angle at various temperatures. (b) The average peak resonance wavelength as a function of temperature. Error bars indicate standard deviation of the wavelength across polarization angles.

5.6 Conclusions

PS-AuNRs were trapped into LC defects of 8CB on surface-treated epoxy pillar arrays. Comparison of different surface treatments showed that homeotropic anchoring induces a plasmon peak shift as the sample was cooled and the LC transitioned from the isotropic to the nematic to the smectic phase sequentially due to the formation of wellordered defects surrounding the pillars. Meanwhile, planar anchoring induced random defect structures, resulting in indistinguishable plasmon peaks with no peak shift as the sample is cooled. Comparison of pillars with different aspect ratios showed that samples with AR = 1.3 exhibited a higher peak shift than samples with AR = 0.9, while no peaks were observed for those with AR = 1.6; this was found correlated to the defect ring structure in the nematic phase. Polarization-resolved optical measurements show that the plasmonic peak resonance wavelength was not affected by the angle of light polarization due to the circular symmetry of the micropillar arrays. Dispersing PS-AuNRs in LCs in a flat homeotropic cell induced rod aggregation and a suppression of the plasmon resonance response. The ensemble assembly and actuation of PS-AuNRs demonstrated is achieved through several factors, including 1) the surface functionalization of AuNRs with PS brushes allowing for dispersion in 8CB without aggregation, 2) the control over the surface topography at a microscale, 3) the manipulation of the LC surface anchoring through surface functionalization to form well-ordered defect structures, and 4) the reversible compression of the LC director field tuned by temperature. Precise control over the surface properties of all the components in the system leads to reversible coupling of the PS-AuNRs and large plasmon peak shifts. This effect can be applied for enhanced and selective sensing applications.

5.7 Contributions

Lee, E.,[†] Ferrier, R. C.,[†] Xia, Y.,[†] Kim, H.-N., Gharbi, M. A., Kamien, R. D., Stebe, K. J., Composto, R. J. and Yang, S. "Self assembly and actuation of gold nanorods in liquid

crystals for tunable plasmon resonance." Manuscript in preparation. ([†]Equal contribution.)

Lee, E and Kim, H.-N. performed PS-AuNR assemblies in liquid crystal/micropillar experiments. Ferrier, R.C. performed gold nanorod synthesis and functionalization. Xia, Y. and Gharbi, M. A. performed earlier experiments and simulation of LC assemblies in micropillar arrays. The observations of LC defect ring structures and ring compression depending on pillar aspect ratio and spacing inspired the study of AuNR assembly in LC/micropillar arrays.

5.8 References

- 1 Karker, N., Dharmalingam, G. & Carpenter, M. A. Thermal energy harvesting plasmonic based chemical sensors. *ACS Nano* **8**, 10953, doi:10.1021/nn504870b (2014).
- 2 Gormley, A. J., Chapman, R. & Stevens, M. M. Polymerization amplified detection for nanoparticle-based biosensing. *Nano Lett* **14**, 6368, doi:10.1021/nl502840h (2014).
- 3 Young, K. L. *et al.* Using DNA to design plasmonic metamaterials with tunable optical properties. *Advanced Materials* **26**, 653, doi:10.1002/adma.201302938 (2014).
- 4 Zhou, J. *et al.* Interfacial assembly of mussel-inspired au@ag@ polydopamine core–shell nanoparticles for recyclable nanocatalysts. *Advanced Materials* **26**, 701, doi:10.1002/adma.201303032 (2014).
- 5 Nikoobakht, B. & El-Sayed, M. A. Preparation and growth mechanism of gold nanorods (nrs) using seed-mediated growth method. *Chemistry of Materials* **15**, 1957, doi:10.1021/cm020732l (2003).
- 6 Sau, T. K. & Murphy, C. J. Seeded high yield synthesis of short au nanorods in aqueous solution. *Langmuir* **20**, 6414, doi:10.1021/la049463z (2004).
- 7 Ferrier, R. C. *et al.* Gold nanorod linking to control plasmonic properties in solution and polymer nanocomposites. *Langmuir* **30**, 1906, doi:10.1021/la404588w (2014).
- 8 Hore, M. J. A. & Composto, R. J. Nanorod self-assembly for tuning optical absorption. *ACS Nano* **4**, 6941, doi:10.1021/nn101725j (2010).
- 9 Nie, Z. *et al.* Self-assembly of metal-polymer analogues of amphiphilic triblock copolymers. *Nature Materials* **6**, 609, doi:10.1038/nmat1954 (2007).

- 10 Zhao, D., Zhang, Z., Wen, Y., Zhang, X. & Song, Y. Reversible gold nanorod assembly triggered by ph-responsive DNA nanomachine. *Applied Physics Letters* 102, 123101, doi:10.1063/1.4798513 (2013).
- 11 Sethi, M., Joung, G. & Knecht, M. R. Linear assembly of au nanorods using biomimetic ligands. *Langmuir* **25**, 1572, doi:10.1021/la802845b (2009).
- 12 Funston, A. M., Novo, C., Davis, T. J. & Mulvaney, P. Plasmon coupling of gold nanorods at short distances and in different geometries. *Nano Lett* **9**, 1651, doi:10.1021/nl900034v (2009).
- 13 Qian, X., Li, J. & Nie, S. Stimuli-responsive sers nanoparticles: Conformational control of plasmonic coupling and surface raman enhancement. *Journal of the American Chemical Society* **131**, 7540, doi:10.1021/ja902226z (2009).
- 14 Nikoobakht, B. & El-Sayed, M. A. Surface-enhanced raman scattering studies on aggregated gold nanorods[†]. *The Journal of Physical Chemistry A* **107**, 3372, doi:10.1021/jp026770+ (2003).
- 15 Ferrier, R. C., Jr. *et al.* Gold nanorod linking to control plasmonic properties in solution and polymer nanocomposites. *Langmuir* **30**, 1906, doi:10.1021/la404588w (2014).
- 16 Umadevi, S., Feng, X. & Hegmann, T. Large area self-assembly of nematic liquid-crystal-functionalized gold nanorods. *Advanced Functional Materials* 23, 1393, doi:10.1002/adfm.201202727 (2013).
- 17 De Sio, L. *et al.* All-optical control of localized plasmonic resonance realized by photoalignment of liquid crystals. *Journal of Materials Chemistry C* **1**, 7483, doi:10.1039/C3TC31733A (2013).
- 18 De Sio, L. *et al.* Double active control of the plasmonic resonance of a gold nanoparticle array. *Nanoscale* **4**, 7619 (2012).
- 19 Dickson, W., Wurtz, G. A., Evans, P. R., Pollard, R. J. & Zayats, A. V. Electronically controlled surface plasmon dispersion and optical transmission through metallic hole arrays using liquid crystal. *Nano Lett* **8**, 281, doi:10.1021/nl072613g (2008).
- 20 Hao, Q. *et al.* Frequency-addressed tunable transmission in optically thin metallic nanohole arrays with dual-frequency liquid crystals. *Journal of Applied Physics* **109**, 084340, doi:10.1063/1.3581037 (2011).
- 21 Hsiao, V. K., Zheng, Y. B., Juluri, B. K. & Huang, T. J. Light-driven plasmonic switches based on au nanodisk arrays and photoresponsive liquid crystals. *Advanced Materials* **20**, 3528, doi:10.1002/adma.200800045 (2008).
- 22 Liu, Q. *et al.* Shape-dependent dispersion and alignment of nonaggregating plasmonic gold nanoparticles in lyotropic and thermotropic liquid crystals. *Phys Rev E* **89**, 052505, doi:10.1103/PhysRevE.89.052505 (2014).
- Liu, Q., Yuan, Y. & Smalyukh, I. I. Electrically and optically tunable plasmonic guest–host liquid crystals with long-range ordered nanoparticles. *Nano Lett* 14, 4071, doi:10.1021/nl501581y (2014).
- 24 Lopez-Leon, T., Fernandez-Nieves, A., Nobili, M. & Blanc, C. Nematic-smectic transition in spherical shells. *Phys Rev Lett* **106**, 247802, doi:10.1103/PhysRevLett.106.247802 (2011).

- 25 Senyuk, B. *et al.* Shape-dependent oriented trapping and scaffolding of plasmonic nanoparticles by topological defects for self-assembly of colloidal dimers in liquid crystals. *Nano Lett* **12**, 955, doi:10.1021/nl204030t (2012).
- 26 Miguez, H. *et al.* Mechanical stability enhancement by pore size and connectivity control in colloidal crystals by layer-by-layer growth of oxide. *Chem Commun*, 2736, doi:10.1039/B208805N (2002).
- 27 Cavallaro, M. *et al.* Exploiting imperfections in the bulk to direct assembly of surface colloids. *Proceedings of the National Academy of Sciences of the United States of America* **110**, 18804, doi:10.1073/pnas.1313551110 (2013).
- 28 DiDonna, B. A. & Kamien, R. D. Smectic blue phases: Layered systems with high intrinsic curvature. *Phys Rev E* **68**, 041703, doi:10.1103/PhysRevE.68.041703 (2003).
- 29 Honglawan, A. *et al.* Topographically induced hierarchical assembly and geometrical transformation of focal conic domain arrays in smectic liquid crystals. *Proceedings of the National Academy of Sciences* **110**, 34, doi:10.1073/pnas.1214708109 (2013).
- 30 Picano, F., Hołyst, R. & Oswald, P. Coupling between meniscus and smectic-a films: Circular and catenoid profiles, induced stress, and dislocation dynamics. *Phys Rev E* **62**, 3747, doi:10.1103/PhysRevE.62.3747 (2000).

CHAPTER 6: Summary and Outlook

6.1 Summary

6.1.1 Smart window fabrication and actuation

Facile fabrication and mechanical actuation of smart windows are demonstrated using tilted pillar arrays confined by mechanically induced wrinkles¹ and transparent films embedded with refractive-index-matching quasi-amorphous silica arrays.² The design of the structures demonstrated in this thesis offers a simple and low-cost approach to dynamically and dramatically change optical properties. Longer oxygen plasma treatment time of PDMS substrates pre-patterned with micropillar arrays increases the amplitude and periodicity of the wrinkles such that each wrinkle could accommodate two pillars, tilting them in varying directions depending on the pre-stretch angle vs. lattice axis. When mechanically stretched, the hierarchical film can reversibly 1) flatten the microwrinkles, 2) reduce the tilt of the pillars, 3) increase the pillar pitch, and thus, 4) offer a wide range of optical tunability ranging from opaqueness (from tilted pillars) to grating color (from straight pillar array) to increasing transparency (from pillars at a larger pitch). While this approach achieves a reversible visual effect between colorful, white, and transparent states, there was no control over the film color and the resting state of the film was opaque.

To achieve an initially transparent smart window with color control upon actuation, a thin layer of quasi-amorphous array of silica nanoparticles (NPs) is embedded in bulk elastomeric PDMS. The film can be reversibly switched from a highly transparent state (90% transmittance in the visible region) to opaqueness (30% transmittance), and display angle-independent reflective colors through mechanical stretching and release. The displayed colors are found dependent only on the NP size not the stretching strain or viewing angle, unlike previously reported literatures. The dramatic change of optical responses is attributed to an increase of diffused light scattering and absorption resulting from the formation of microwrinkles and voids during stretching. The sprayed NPs are quasi-amorphous, therefore, much more robust against stretching in comparison to highly ordered colloidal crystals. The film can withstand repeated stretching and releasing (at least 1000 cycles).

6.1.2 Control of liquid crystal defect structures for directed self-assembly and actuation

By controlling surface topography and interfacial chemistry to manipulate the boundary conditions within micro- and nano-structures, we demonstrate large-scale assembly of microscale LC molecules and their defect structures for potential applications, including the actuation of micro-scale LCEs and dynamic tuning of surface plasmonic resonance. Landau-de-Gennes numerical modeling is employed to show that vertical alignment of LC monomers could only be achieved within PDMS porous membrane (the mold) with planar anchoring, with or without an external magnetic field. When coating the surface the PDMS porous membrane with a thin layer of poly(2-hydroxyethyl methacrylate), the mold surface is switched from hydrophobic to hydrophilic, and thus leading to highly uniform mono-domains of LC alignment along the film thickness. After cross-linking the aligned LCMs, the LC director field is maintained. A large radial strain (30%) across T_{NI} is shown compared to almost no change in LC elastomer micropillars fabricated from untreated molds.

Armed by the understanding of LC surface anchoring and director field in confinement, we investigate the self-assembly and actuation of PS-AuNRs into LC defect structures imposed by the micropillars and boundary conditions. By exploiting the confinement of the smectic-A LC, 8CB, to epoxy micropillar arrays, defects can be formed at precise locations around each pillar, and tuned by varying the aspect ratio of the pillars and the temperature of the system. Comparison of different surface treatments shows that homeotropic LC anchoring on pillar surface induces a surface plasmon peak shift as the sample is cooled and the LC transitions from the isotropic to the nematic to the smectic phase due to the formation of well-ordered defects to the LCs. The dimensions of the defect structure and consequently, the nanorod assembly and its plasmon peak can be altered by reversible heating and cooling cycles at the phase transition temperatures. For homeotropically anchored epoxy pillars with aspect ratio 1.3, the transverse and longitudinal local surface plasmon peak shifts are ~100 and ~153 nm, respectively, much larger than previously reported peak shifts. In comparison, PS-AuNRs/LCs in planar anchoring pillars exhibited reduced plasmon resonance peaks and no shifts with temperature change and PS-AuNRs/LCs in a flat liquid crystal cell with homeotropic anchoring exhibited no plasmon resonance peaks.

6.2 Outlook

The design of hierarchical surface structures demonstrated in this thesis offers a new concept to change a material's physical properties without altering its intrinsic properties. The reversible tilting of PDMS micropillars is used for switching between whiteness, color, and transparency. Besides the change in optical properties, we expect the actuation of the fabricated hierarchical substrates to exhibit unique adhesion and wetting properties due to large changes in the surface roughness.³ Using these substrates, we have studied the morphology of vascular smooth muscle cell and fibroblast using topological and chemical cues (APPENDIX A). Further, the tunable patterns can be prepared from other functional materials, such as LCEs and SMPs which will enhance responsiveness to other stimuli and recyclability. Preliminary studies of engaged complementary SMP micropillars with reversible pillar tilting via wrinkling show enhanced interlocking adhesion.

The use of refractive-index-matching nanoparticles embedded within an elastomer film is simple yet highly versatile and effective method to fabricate tunable transparency windows that can easily be scaled up and commercialized. Preliminary studies show that we can produce films up to 10 cm long, which can be actuated in tandem using rollers with a motor. This system can be extended to other thermoplastic elastomers, e.g. ethylene-vinyl acetate, thermoplastic polyurethane (TPU), and poly(styrene-butadienestyrene) (SBS), and LCE, and nanoparticle systems, e.g. surface-functionalized silica, poly(methyl methacrylate), polystyrene, indium tin oxide, to further enhance mechanical performance and introduce additional functionality in the ultraviolet, near-infrared, and infrared regions. Although smart windows demonstrated here are for control of light transmission, they can also be used in applications such as sensing, displays, camouflage, security encoding, anti-bird collision and heat/solar gain control. Stretched composite smart windows have been preliminary demonstrated for use as projection screens, while they act as transparent films in the un-stretched state. Masks were also used for nanoparticle spraying to encode positive and negative messages within the composite

films. The use of UV-reflective particles within the films may be useful for anti-bird collision applications. The actuation of composite films with such particles may alert birds (which are sensitive to UV reflection and high frequency fluctuations) to the presence of normally transparent windows.⁴⁻⁶

The concept of controlling interfacial chemistry using soft lithography techniques is much simpler and more effective than the use of an external field to direct LC anchoring over a large area, especially in the case of more complex and micro/nanoscale systems, such as porous membranes, channels, and 3D structures. In turn, LC confinement can be applied to fabricate micro- and nanoscale structures for potential applications, including actuators, displays, sensors, dry adhesion, photonic materials, and origami 2D structures to 3D. The nanorod assembly and actuation demonstrated here can be extended to other LC systems (e.g. light responsive LCEs, cholesteric LCs) and particle systems (e.g. quantum dots, titanium dioxide). The use of LCEs would enable the cross-linking of the LC phases with particles embedded within, thereby allowing the fabrication of free-standing solid films which can be actuated and observed using conventional electron microscopy techniques. LCEs exhibit a spontaneous contraction along the director axis when heated above their nematic to isotropic phase-transition temperatures, and the polymer chain changes to a spherical conformation.⁷ Therefore. LCEs have a reversible shape memory effect when triggered by external stimuli, including heat, UV light and electric field.⁸⁻¹² The use of LCEs would therefore enable the actuation of the nanoparticles by multiple stimuli and prevent the aggregation of particles by fixing it within the network structure. The assembly and actuation of quantum dots, such as cadmium selenide nanoparticles, and titanium dioxide particles

using this technique may also lead to novel optical properties, which can be exploited for solar cell applications. The use of indium tin oxide substrates to form the LC cells would allow for electrical actuation of the LC/nanorod system, which is desirable for metamaterial applications.

6.3 References

- 1 Lee, E. *et al.* Tilted pillars on wrinkled elastomers as a reversibly tunable optical window. *Advanced Materials* **26**, 4127, doi:10.1002/adma.201400711 (2014).
- 2 Ge, D. *et al.* A robust smart window: Reversibly switching from high transparency to angle-independent structural color display. *Advanced Materials* **27**, 2489, doi:10.1002/adma.201500281 (2015).
- 3 Lee, E. & Yang, S. Bio-inspired responsive polymer pillar arrays. *MRS Communications* **FirstView**, 1, doi:doi:10.1557/mrc.2015.18 (2015).
- 4 Jones, M. P., Pierce, K. E., Jr. & Ward, D. Avian vision: A review of form and function with special consideration to birds of prey. *Journal of Exotic Pet Medicine* **16**, 69, doi:10.1053/j.jepm.2007.03.012.
- 5 Milius, S. Collision course: Scientists struggle—to make windows safer for birds. *Science News* **184**, 20, doi:10.1002/scin.5591840622 (2013).
- 6 Ödeen, A. & Håstad, O. The phylogenetic distribution of ultraviolet sensitivity in birds. *BMC Evolutionary Biology* **13**, 36, doi:10.1186/1471-2148-13-36 (2013).
- Jin, L. H., Lin, Y. & Huo, Y. Z. A large deflection light-induced bending model for liquid crystal elastomers under uniform or non-uniform illumination. *Int J Solids Struct* 48, 3232, doi:10.1016/j.ijsolstr.2011.07.015 (2011).
- 8 Ohm, C., Brehmer, M. & Zentel, R. Liquid crystalline elastomers as actuators and sensors. *Advanced Materials* **22**, 3366, doi:10.1002/adma.200904059 (2010).
- 9 Cui, J. *et al.* Bioinspired actuated adhesive patterns of liquid crystalline elastomers. *Advanced Materials* **24**, 4601, doi:10.1002/adma.201200895 (2012).
- 10 Liu, D., Bastiaansen, C. W. M., den Toonder, J. M. J. & Broer, D. J. Photoswitchable surface topologies in chiral nematic coatings. *Angewandte Chemie International Edition* **51**, 892, doi:10.1002/anie.201105101 (2012).
- 11 Urayama, K., Honda, S. & Takigawa, T. Deformation coupled to director rotation in swollen nematic elastomers under electric fields. *Macromolecules* **39**, 1943, doi:10.1021/ma052762q (2006).
- 12 van Oosten, C. L., Bastiaansen, C. W. M. & Broer, D. J. Printed artificial cilia from liquid-crystal network actuators modularly driven by light. *Nature Materials* 8, 677, doi:10.1038/nmat2487 (2009).

APPENDIX A: Guiding cell morphology using

topological and chemical cues

Elaine Lee, Yu Xia, Kaori Ihida-Stansbury, Shu Yang. Manuscript in preparation.

A.1 Introduction

Pulmonary arterial hypertension (PAH) is characterized by vascular remodeling, including the hyperplasia and hypertrophy of smooth muscle cells (SMCs). This causes the medial thickening of lung arteries, resulting in pulmonary vascular resistance, high blood pressure and leading to right ventricular dysfunction and heart failure within 2 years without treatment.¹ As shown by previous work done in Dr. Kaori Ihida Stansbury's lab, the ultrastructure of the artery matrix is greatly altered by PAH. Healthy artery matrix is composed of well-organized fibers (Figure A.1a), while diseased PAH arterial matrix exhibits random fiber alignment (Figure A.1b). In addition, the adventitial layer (outermost connective tissue covering) of the artery, which has been implicated as the modulator of arterial remodeling, thickens with increased cellularity and extracellular (ECM) deposition. Hypoxic animal models of PAH showed increased production of fibroblasts, expression of contractile proteins (e.g. α -smooth muscle actin) in fibroblasts, and differentiation to myofibroblasts.²⁻⁴ The transition of fibroblasts to myofibroblasts, increased myofibroblast proliferation, myofibroblast apoptosis, myofibroblast migration into the intima, adventitial fibrosis, and expression of matrix metalloproteinases (MMPs) all contribute to structural changes in the vascular wall.²⁻⁴ Additionally, previous studies have shown that the extracellular matrix (ECM) glycoprotein, Tenascin-C (Tn-C), is

highly expressed in PAH tissues, promoting vascular SMC proliferation, fibroblast migration, and angiogenesis.⁵



Figure A.1 SEM images of (a) normal artery matrix and (b) pulmonary arterial hypertension artery matrix. Scale bar: 10 μ m. Images provided by Dr. Kaori Ihida-Stansbury.

This begs the question of whether the fiber orientation of the ECM plays a role in arterial cell alignment, and therefore cell morphology, behavior, and proliferation as well as PAH vascular wall remodeling. The cell has been described as "an integrated mechanochemical sensory system" which probes the surrounding environment by adhering to the ECM, spreading over the substrate, and contracting the cytoskeleton.⁶ Cytoskeleton contraction leads to stresses at the focal adhesions, which then traduce the stresses into regulatory signals causing changes in the ECM. ECM stiffness regulates stem cell fate via cytoskeletal alterations. Cells are also sensitive to the anisotropy of the substrate texture, which can cause cell alignment, elongation, and directional migration. Although it is well-established that cells respond to the surface chemistry and stiffness of their substrates, the spatiotemporal coordination and mechano-transduction of extracellular mechanics into cellular regulation and signaling is not well-quantified and understood. Although previous studies have shown that spatiotemporal cues elicit various

cell behavior, changes in cell morphology, and the guiding of cell fate and differentiation, little has been studied in relation to the pathogenesis. In this study, we hope to elucidate the effect of ECM properties on SMC and fibroblast behavior in PAH using synthetic substrates to mimic the healthy and diseased ECM environment.

In recent years, microfabrication methods, such as microcontact printing and capillary force lithography, have been developed to fabricate patterned substrates for cellular studies with better spatiotemporal control over the surface chemistry and topography. Through the use of platforms such as elastomeric micropillars,⁷ hydrogels,⁸ nanogrooves,⁹ it has been shown that cell morphology and function can be regulated by the substrate stiffness and topography, an analog to the ECM microenvironment. Of these, micropillar arrays circumvent the limitations of previously reported techniques involving continuous substrates, and offer precise control of the compliance of the underlying substrates for cellular studies.⁷ In a micropillar array, the multidirectional mechanical forces exerted by a cell can be isolated to each individual pillar and measured independently and collectively. Alternatively, nanogrooves have been shown to guide cell spreading and alignment.⁹ Here, the mechanically tunable wrinkling instability in PDMS was exploited to create a series of substrates to study cell differentiation of human SMCs and fibroblasts, including a 1D sinusoidal wavy wrinkle structure, a 2D pillar array and a composite structure that combines wrinkles with a 2D pillar array. Periodically ordered wrinkle structures were fabricated by mechanical stretching and release of oxidized PDMS, as described in Chapter 2.4. These hierarchically patterned substrates were used to survey cell behavior and morphologies and it was shown that cells align along the wrinkle direction. However, the introduction of pillars or Tn-C masked the wrinkle

geometry, resulting in a less elongated morphology in the case of SMCs. In addition, cells on wrinkles with pillars or Tn-C exhibited longer filopodia, which suggests that the cells were continuously probing the surrounding geometry.

A.2 Experimental methods

A.2.1 Fabrication of PDMS Pillar Array

The PDMS pillar array was replica molded from an epoxy master following the procedure reported earlier.¹⁰ Briefly, PDMS precursor (Sylgard 184, Dow Corning) was mixed with a curing agent in a 10:1 weight ratio and degassed in a vacuum chamber for 1 hour. The mixture was poured over the epoxy pillar master (1 µm diameter, 2 µm pitch, 4 µm height) and cured at 65°C for 4 h. The resulting PDMS membrane was treated with UVO for 1 hour. followed by deposition of vapor tridecafluorotetrahydrooctyltrichlorosilane (SIT8174.0, Gelest) as a release agent overnight to render the surface hydrophobic. Another degassed mixture of PDMS precursor with 10 wt% curing agent was poured over the treated PDMS membranes and cured at 100°C overnight. After cooling to room temperature, the PDMS pillar array was peeled from the mold.

A.2.2 Surface wrinkling of PDMS substrates

The fabrication followed the procedure reported previously.¹¹ Briefly, the molded PDMS film (no pattern, hole array, or pillar array) was clamped and stretched uniaxially (ϵ up to 30%) using a custom-made stretching device. The surface was then treated with oxygen

plasma (Technics, model PE11-A) at a power of 100 watts, pressure of 0.5 torr for1-20 min. Wrinkle patterns formed spontaneously upon release of the strain.

A.2.3 Sample characterization

Scanning electron microscopy (SEM) images were taken by FEI Quanta Field Emission Gun Environmental SEM in high vacuum mode at an acceleration voltage of 5kV after the substrates were sputtered with gold-palladium. The topography of the substrates were examined using a DI Dimension 3000 atomic force microscope (AFM) and images were rendered using WSxM.¹² Transmission spectra were taken using a custom-built freespace microscope with a white light source and normalized to a flat PDMS film.

A.2.4 Cell culture

Human pulmonary artery smooth muscle cells (SMCs) and human fibroblasts (CCD-19Lu) were maintained in Sm-GM-2 culture medium (Lonza), supplemented with growth factors (hEGF, insulin, hFGF-B, FBS and gentamicin/amphotericin B), and were cultured at 37°C in a humidified atmosphere with 5% CO₂ until seeded onto PDMS substrate for cellular experiments.

A.2.5 Cell seeding

PDMS substrates were exposed to UV to render the surface hydrophilic, washed with phosphate buffered saline (PBS) solution and coated with 0.2mg/mL collagen I (Pure Col) at 4°C overnight. After washing with PBS several times, cells were seeded on the substrates at a concentration 1 x 10^4 cells/cm² in cell culture media and incubated at 37°C in a humidified atmosphere with 5% CO₂ until processed for further examination.

A.2.6 SEM pre-processing

Decellularized tissue and cells cultured on PDMS substrates were fixed in 2% glutaraldehyde containing 0.1M cacodylate buffer, dehydrated in ethanol diluted distilled water at intervals of increasing ethanol content until 100%. The substrates were then critically dried or chemically dried using hexamethyldisiloxane (HMDS). Dried specimens were then sputtered with palladium/gold for imaging using SEM.

A.2.7 Immunofluorescence Staining

Cells cultured on PDMS substrates were rinsed with PBS fixed with 4% paraformaldehyde diluted in PBS. After washing with PBS, cells were then permeabilised with 0.2% triton X-100 to block non-specific IgG binding and then incubated with primary antibodies. Anti- α -smooth muscle actin (SMA) (Sigma-Aldrich) was used for SMC differentiation state and anti- Ki67 was used to detect proliferating cells. Following th primary antibody incubation, cells were incubated with species-specific fluorescent-conjugated antibodies (Molecular Probes Inc) for antigen detection. DAPI (KPL) staining was applied for nuclear staining. Specimens were then mounted using mounting medium (KPL) and examined using a Nikon 90i fluorescence microscope and analyzed using NIS-Elements AR, ImageJ software and/or Matlab.

A.3 Smooth muscle cells

Since cells respond to both biochemical and mechanical signals, it is essential to control the surface/bulk chemistry and the mechanical properties of the substrates used for cellular studies.⁷ Here, PDMS was chosen as the base substrate due to its low elastic modulus, allowing reversible mechanical deformation up to 30% strain. By using

micropatterned substrates, the topography and compliance can be tuned by altering the micropillar and wrinkle dimensions without changing the surface chemistry. From a flat PDMS film, regular wrinkles formed perpendicularly to the stretch direction with wavelength of 2 μm (**Figure A.2a**). Wrinkles combined with pillars were fabricated as described in Chapter 2.4 (**Figure A.2e**). On wrinkle-only PDMS substrates, smooth muscle cells were found to align along the wrinkle direction, i.e. perpendicular to the stretch direction (**Figure A.2b**, **d**), suggesting that cell spreading is guided by the topography of the substrate. The results were consistent with literature reporting the nanogroove-induced alignment of fibroblasts¹³ and glioma cells.¹⁴ However, when SMCs were seeded on the composite wrinkle substrates, i.e. pillars on top of the wrinkles, cells exhibit a less elongated morphology (**Figure A.2f, h**), suggesting that the pillars masked the underlying surface wrinkle geometry. Higher magnifications show that cells on wrinkles with pillars exhibited longer filopodia, suggesting that the cells were still probing the pillar environment (**Figure A.2e, g**).^{15,16}



Figure A.2 SEM images of wrinkled PDMS from (a) a flat film, and (e) a square pillar array. SEM and fluorescence microcopy images of smooth muscle cells cultured on (b-d) wrinkled PDMS, and (f-h) wrinkled PDMS with a pillar array. Higher magnifications

show that cells on wrinkles (c) have shorter filopodia than cells on wrinkles with pillars (g). All substrates were coated with collagen. Red arrows indicate stretch direction. Yellow arrows indicate filopodia. Cell culture data provided by Dr. Kaori Ihida-Stansbury.

In comparison with cells seeded on wrinkle-only substrates coated with collagen, random alignment of SMCs was observed on wrinkles coated with Tenascin-C (Tn-C) (**Figure A.3a**), suggesting that both surface geometry and chemistry affect SMC behaviors. Long filopodia were observed at high magnification (**Figure A.3b**), suggesting that SMCs were unable to sense the underlying wrinkle substrate when it was coated by Tn-C.



Figure A.3 SEM images of smooth muscle cells cultured onto wrinkled PDMS coated with Tenascin-C at (a) low and (b) high magnifications. Data provided by Dr. Kaori Ihida-Stansbury.

A.4 Fibroblasts

While PAH is often characterized by the hyperplasia and hypertrophy of smooth muscle cells, recent research has shown that fibroblasts also play a vital role in the vascular wall modeling.² Found primarily in the adventitial layer, fibroblasts can dramatically alter the production of ECM proteins in response to stress or injury. Pathological studies have shown that PAH legions are accompanied by excessive ECM proteins, such as collagen, elastin, fibronectin, and Tn-C. In turn, these proteins are associated with fibroblast proliferation and transition into myofibroblasts.³ Therefore, it is important to understand the role of fibroblasts in the progression of PAH, which I have

pursued by using synthetically fabricated substrates to mimic the ECM. Using a similar procedure as SMCs, human lung fibroblasts (CCD-19Lu, ATCC) were cultured onto PDMS substrates with various topography, including flat substrates, wrinkles with low amplitude, wrinkles with high amplitude, and micropillars, and coated with either collagen or Tn-C (**Figure A.4a-c**). As shown by fluorescence microscopy, fibroblasts are randomly aligned on bare PDMS (**Figure A.4d**) and substrates patterned with micropillars (**Figure A.4e**). On wrinkled substrates, the cells align along the wrinkle direction (**Figure A.4f-g**). Image analysis indicates that cells cultured on flat or pillar substrates show a broad distribution of cell direction with respect to the horizontal (**Figure A.4h**, red and black) while more than 90% of cells on wrinkles align within 20° of the wrinkle direction (**Figure A.4h**, blue, turquoise and pink). While cells are aligned on wrinkles of both low (~250 nm) and high (~750 nm) amplitude, cells exhibited much more elongation on wrinkles of high amplitude with aspect ratios of up to 35.



Figure A.4 SEM images of PDMS with (a) pillars with diameter 1 μ m, pitch 2 μ m, and aspect ratio 4, (b) wrinkles with amplitude ~250 nm, (c) wrinkles with amplitude ~750 nm. Scale bars 4 μ m. Fluorescence images of human fibroblasts CCD19-Lu cultured on PDMS with (d) no pattern, (e) pillars with diameter 1 μ m, pitch 2 μ m, and aspect ratio 4, (f) wrinkles with amplitude ~250 nm, and (g) wrinkles with amplitude ~750 nm. Scale bars 100 μ m. All substrates were coated with collagen. Arrows indicate wrinkle direction. Distribution of cell (h) alignment and (i) elongation. Abbreviations: Col = collagen coated, F = flat, P = pillar, W = wrinkle, WP = wrinkles with pillars, # = oxygen plasma treatment time.

In contrast to SMCs, fibroblasts cultured on substrates coated with Tn-C did not show obvious differences in cell alignment and elongation (**Figure A.5a-g**) compared to those cultured on substrates coated with collagen. Fibroblasts cultured on wrinkles coated with Tn-C also exhibited over 90% alignment within 20° of the wrinkle direction (**Figure A.5h**) with elongations of up to 15 (**Figure A.5i**).



Figure A.5 SEM images of PDMS with (a) pillars with diameter 1 μ m, pitch 2 μ m, and aspect ratio 4, (b) wrinkles with amplitude ~250 nm, (c) wrinkles with amplitude ~750 nm. Scale bars 4 μ m. Fluorescence images of human fibroblasts CCD19-Lu cultured on PDMS with (d) no pattern, (e) pillars with diameter 1 μ m, pitch 2 μ m, and aspect ratio 4, (f) wrinkles with amplitude ~250 nm, and (g) wrinkles with amplitude ~750 nm. Scale bars 100 μ m. All substrates were coated with Tenascin-C. Arrows indicate wrinkle direction. Distribution of cell (h) alignment and (i) elongation. Abbreviations: Tn-C = Tn-C coated, F = flat, P = pillar, W = wrinkle, WP = wrinkles with pillars, # = oxygen plasma treatment time.

Following initial studies showing that cells preferred alignment along onedimensional wrinkles, a series of wrinkle substrates with controlled dimensions were fabricated by varying the oxygen plasma treatment time of pre-stretched PDMS membranes (**Table A.1**). The AFM images of the wrinkle topography are shown in **Figure A.6a-d**. By taking cross-sectional profiles of the AFM images (**Figure A.6e**), the wrinkle amplitude and wavelength was deduced. The fabrication conditions and resulting wrinkle dimensions are summarized in **Table A.1**. The wrinkles were then either coated with collagen or Tn-C and fibroblasts were cultured atop the wrinkles (**Figure A.7**).

Table A.1. Summary of the fabrication conditions of PDMS wrinkles and their resulting dimensions, amplitude and wavelength.

Oxygen Plasma Treatment Time (min)	Amplitude (µm)	Wavelength(µm)
1	0.25	0.9
5	0.35	1.2
10	0.5	1.6
20	0.7	2.5



Figure A.6 AFM images of wrinkles fabricated by pre-stretching PDMS by 30% strain and treating with oxygen plasma (P = 100W; p=0.5 torr) for (a) 1, (b) 5, (c) 10, and (d) 20 min. (e) Profiles of the corresponding AFM images (# = oxygen plasma treatment time).



Figure A.7 Fluorescence images of human fibroblasts CCD19-Lu cultured on PDMS wrinkles with amplitude of about (a, e) 250, (b, f) 350, (c, g) 500, and (d, h) 750 nm. The wrinkles were coated with (a-d) collagen and (e-h) Tenascin-C.

Image analysis was then used to calculate the aspect ratio (=length/width) (**Figure A.8**) and alignment of the cells (**Figure A.9**). No significant differences in the cell elongation were found for substrates with different dimensions and coatings. However, the number of cells found on Tn-C substrates was lower, especially on lower aspect ratio wrinkles.



Figure A.8 Frequency distribution of aspect ratio of fibroblasts cultured on PDMS wrinkles. Abbreviations: COL = collagen coated, TN-C = Tenascin-C coated, W = wrinkle, # = oxygen plasma treatment time.



Figure A.9 Angular distribution of human fibroblasts CCD19-Lu cultured on PDMS wrinkles with amplitude of about (a, e) 250, (b, f) 350, (c, g) 500, and (d, h) 750 nm. The wrinkles were coated with (a-d) collagen and (e-h) Tenascin-C.

The cell orientation of the fibroblasts on collagen-coated wrinkles appeared to depend on the wrinkle amplitude, while that of those on Tn-C-coated wrinkles did not. To further study the effect of the surface coating, image processing was used to analyze the fluorescence of the cells stained for α -smooth muscle actin (α -SMA) expression (**Figure A.10**). All substrates coated with Tn-C exhibited higher α -SMA expression, indicating that the fibroblasts on the Tn-C-coated substrates are in a more contractile state.



Figure A.10 Fluorescence optical microscopy images of fibroblasts stained for α -SMA cultured on PDMS wrinkles coated with (a) collagen and (b) Tn-C. (c) Fluorescence intensity of fibroblasts cultured on PDMS wrinkles stained for α -SMA.

A.5 Conclusions and Outlook

A series of PDMS substrates was fabricated to study the effect of surface topography, including flat, microwrinkles with various dimensions, and microwrinkles with pillars, and chemistry, including collagen and Tn-C, on the behavior of vascular smooth muscle cells and fibroblasts. We showed that the alignment of vascular SMCs and fibroblasts could be guided by the topography of the underlying substrate. In particular, cells preferred to align and elongate along one-dimensional wrinkle substrates of higher amplitude and treated with collagen. This topography could be masked by the addition of high aspect ratio features on the surface, inhibiting the alignment of SMCs and fibroblasts. In the case of SMCs, altering the ECM composition, such as coating of Tn-C, altered the cells' ability to sense the substrate and align along the topography. In the case of fibroblasts, Tn-C coating on the substrates did not appear to affect the alignment of the cells. However, cells on such substrates exhibited much higher α -SMA expression, indicating that they are in a much more contractile state. Since Tn-C is overexpressed in the ECM in PAH arteries, our results imply that PAH cells may be a more contractile state, leading to vascular remodeling. This begs the question of whether the morphology of PAH cells can be altered using artificial substrates to reverse the diseased state. Further studies using PAH patient cells on artificial substrates, such as those reported here, are needed to further elucidate the relationship between the cells' health state, the artificial ECM environment, and the cells' ability to sense and adapt to the ECM.

A.6 References

- 1 Sakao, S., Tatsumi, K. & Voelkel, N. F. Reversible or irreversible remodeling in pulmonary arterial jypertension. *American Journal of Respiratory Cell and Molecular Biology* **43**, 629, doi:10.1165/rcmb.2009-0389TR (2010).
- Strauss, B. H. & Rabinovitch, M. Adventitial fibroblasts defining a role in vessel wall remodeling. *American Journal of Respiratory Cell and Molecular Biology* 22, 1, doi:10.1165/ajrcmb.22.1.f172 (2000).

- 3 Stenmark, K. R., Davie, N., Frid, M., Gerasimovskaya, E. & Das, M. Role of the adventitia in pulmonary vascular remodeling. *Physiology* **21**, 134, doi:10.1152/physiol.00053.2005 (2006).
- 4 Humphrey, J. D. Mechanisms of arterial remodeling in hypertension: Coupled roles of wall shear and intramural stress. *Hypertension* **52**, 195, doi:10.1161/hypertensionaha.107.103440 (2008).
- 5 Jones, P. L. & Rabinovitch, M. Tenascin-c is induced with progressive pulmonary vascular disease in rats and is functionally related to increased smooth muscle cell proliferation. *Circulation Research* **79**, 1131, doi:10.1161/01.RES.79.6.1131 (1996).
- 6 Raghavan, S. & Chen, C. S. Micropatterned environments in cell biology. *Advanced Materials* **16**, 1303, doi:10.1002/adma.200400594 (2004).
- 7 Tan, J. L. *et al.* Cells lying on a bed of microneedles: An approach to isolate mechanical force. *Proceedings Of The National Academy Of Sciences Of The United States Of America* **100**, 1484, doi:10.1073/pnas.0235407100 (2003).
- 8 Kim, J., Yoon, J. & Hayward, R. C. Dynamic display of biomolecular patterns through an elastic creasing instability of stimuli-responsive hydrogels. *Nature Materials* **9**, 159, doi:10.1038/Nmat2606 (2010).
- 9 Park, J., Kim, H. N., Kim, D. H., Levchenko, A. & Suh, K. Y. Quantitative analysis of the combined effect of substrate rigidity and topographic guidance on cell morphology. *IEEE T Nanobiosci* **11**, 1, doi:10.1109/TNB.2011.2165728 (2011).
- 10 Zhang, Y., Lo, C.-W., Taylor, J. A. & Yang, S. Replica molding of high-aspectratio polymeric nanopillar arrays with high fidelity. *Langmuir* 22, 8595, doi:10.1021/la061372+ (2006).
- 11 Lin, P. C. & Yang, S. Spontaneous formation of one-dimensional ripples in transit to highly ordered two-dimensional herringbone structures through sequential and unequal biaxial mechanical stretching. *Applied Physics Letters* **90**, 241903, doi:10.1063/1.2743939 (2007).
- 12 Horcas, I. *et al.* Wsxm: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* **78**, 013705, doi:10.1063/1.2432410 (2007).
- 13 Loesberg, W. A. *et al.* The threshold at which substrate nanogroove dimensions may influence fibroblast alignment and adhesion. *Biomaterials* **28**, 3944, doi:10.1016/j.biomaterials.2007.05.030 (2007).
- 14 Zhu, B. *et al.* Nanotopographical guidance of c6 glioma cell alignment and oriented growth. *Biomaterials* **25**, 4215, doi:10.1016/j.biomaterials.2003.11.020 (2004).
- 15 Albrecht-Buehler, G. Filopodia of spreading 3t3 cells. Do they have a substrateexploring function? *J Cell Biol* **69**, 275, doi:10.1083/jcb.69.2.275 (1976).
- Dalby, M. J., Gadegaard, N., Riehle, M. O., Wilkinson, C. D. W. & Curtis, A. S. G. Investigating filopodia sensing using arrays of defined nano-pits down to 35 nm diameter in size. *Int J Biochem Cell B* 36, 2005, doi:10.1016/j.biocel.2004.03.001 (2004).

APPENDIX B: List of Publications

- Lee, E.,[†] Ferrier, R. C.,[†] Xia, Y.,[†] Gharbi, M. A., Stebe, K. J., Kamien, R. D., Composto, R. J. and Yang, S. "Self assembly and actuation of gold nanorods in liquid crystals for tunable plasmon resonance." Manuscript in preparation. ([†]Equal contribution.)
- Xia, Y., Lee, E., Hu, H., Gharbi, M. A., Beller, D.A., Fleischmann, E., Kamien, R. D., Zentel, R. and Yang, S. "Control of liquid crystal anchoring in liquid crystal elastomer pillar arrays by interfacial chemistry." Manuscript in preparation.
- Lee, E., Yang, S. "Bio-inspired Responsive Polymer Pillar Arrays." MRS Commun., 2015, Accepted. (Invited Perspective on Polymers/Soft Matter)
- Ge, D.[†] and Lee, E.,[†] Yang, L., Cho, Y., Li, M., Gianola, D.S., and Yang, S. "A robust smart window: reversibly switching from high transparency to angle-independent structural color display." Adv. Mater., 2015, 27, 2489–2495. ([†]Equal contribution). U.S. Provisional Application No. 62/127,275.
- Zheng, Y., Li, J., Lee, E. and Yang, S. "Light-induced shape recovery of deformed shape memory polymer micropillar arrays with gold nanorods." RSC Advances, 2015, 5, 30495-30499.
- Ge, D., Yang, L., Wang, C., Lee, E and Yang, S. "A multi-functional oil/water separator from a selectively pre-wetted superamphiphobic nanoparticle coated paper," Chem. Comm., 2015, 51, 6149-6152.
- 7. Lee, E., Zhang, M., Cho, Y., Cui, Y., Van der Spiegel, J., Engheta, N. and Yang, S.
 "Tilted pillars on wrinkled elastomers as a reversibly tunable optical window", Adv.
 Mater. 2014, 26 (24), 4127–4133