

THE APPLICATIONS FOR 3D INVERSE OPAL MICROSTRUCTURES

BY

TAE WAN KIM

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Materials Science and Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2011

Urbana, Illinois

Advisor:

Professor Paul V. Braun

Abstract

Three-dimensional micro structures have been great interest to many scientists due to their useful properties. In this thesis, I show some examples of these 3-D micro structures applications, and in particular 3-D inverse opal micro structures made using spherical colloidal nanoparticles as building blocks. Because the interactions between colloidal particles are well understood and they are easy to synthesize, they have been widely used to grow these 3-D periodic structures. This inverse opal micro structure can not only be used for micro electromechanical systems (MEMS) devices, but also it can be useful in designing a dye-sensitized solar cell (DSSC). The first chapter will demonstrate the properties of these colloidal particles and explain the fabrication process of 2-D and 3-D colloidal microstructures. The second and third chapter will focus on the MEMS devices and a DSSC in order to show the potentials of these 3-D microstructures for various applications.

To my family

ACKNOWLEDGEMENTS

I would like to thank my advisor Professor Paul Braun for supporting me during my graduate studies. He not only gave me the motivation to continue my work but also he guided me and encouraged me with positive criticism. His helpful advice will never be forgotten.

I also thank Xindi Yu for preparing me to perform well in the lab. He taught me the basics of colloidal self-assembly and electro deposition. I show gratitude to his kindness for showing all the procedures in such a short period. He also gave me the opportunity to work with Zhenting Dai, my collaborator.

I received great help from my collaborators especially Zhenting Dai and Yoonho Jun. Many thanks to Zhenting who has been working with me for almost 2 years on the micro cantilever project. He designed the cantilever and measured the mechanical properties of the cantilevers. Also Yoonho, a former postdoc in our group, gave me the opportunity to continue his work on the DSSC project.

I thank my parenst, who raised me in a difficult environment and gave me the chance to study in a great school. They have always been my mentor and good friend even when I was in my worst situation. I love them so much.

Lastly, none of my work would have been possible without the Kevin, Mark, Steven, Augustin, Chunjie, Hailong, Corrisa, the rest of the Braun group, and the EFRC grant: Light Material Interactions in Energy Conversions for their financial support.

.

TABLE OF CONTENTS

Chapter 1 Introduction	1
1.1 Colloids (Colloidal Particles).....	1
1.2 Colloidal Forces and Their Interactions.....	1
1.3 Characterization of the Interactions Between Colloidal Particles.....	3
1.4 Self-Assembly of Colloidal Particles.....	6
1.4.1 Sedimentation.....	6
1.4.2 Vertical Deposition.....	7
1.5 Fabrication of Colloidal-Crystal Thin Film.....	8
1.5.1 Fabrication of Two Dimensional Colloidal-Crystal Structure.....	8
1.5.2 Fabrication of Three Dimensional Colloidal-Crystal Structure.....	9
1.6 Sintering.....	10
1.7 Tables.....	11
1.8 Figures.....	12
1.9 References.....	20
Chapter 2 Micromechanical Devices Having 3-D Inverse Opal Microstructure	26
2.1 Introduction	26
2.2 Nickel Inverse Opal Cantilevers.....	27
2.2.1 The Preparation of Conductive Substrate	27
2.2.2 Colloidal Crystal Growth on Conductive Substrate	27
2.2.3 Electrodeposition.....	28
2.3 Al ₂ O ₃ Microcantilevers.....	29
2.4 The Mechanical Properties of 3-D Dimensional Nickel Inverse Opal Cantilevers.....	30

2.5 Conclusion.....	32
2.6 Experimental.....	32
2.7 Tables.....	35
2.8 Figures.....	36
2.9 References.....	46
Chapter 3 Dye Sensitized Solar Cells Using 3-D Transparent Conductive Oxide.....	48
3.1 Introduction.....	48
3.2 Solar Cells.....	48
3.2.1 Photovoltaics.....	48
3.2.2 Dye Sensitized Solar Cell (DSSC).....	49
3.3 3-D Transparent Conductive Oxide DSSC.....	53
3.3.1 The Preparation of Silica Opal Template.....	53
3.3.2 Tin Oxide Inverse Opal.....	54
3.3.3 Mesoporous Titania.....	54
3.4 Characterization of DSSC.....	55
3.5 Conclusion.....	57
3.6 Experimental.....	58
3.7 Tables.....	60
3.8 Figures.....	61
3.9 References.....	68
Chapter 4 Conclusions.....	69
Author's Biography.....	71

CHAPTER 1

Introduction

1.1 Colloids (Colloidal Particles)

The study of the self-assembly of colloidal particles has been a great interest to many scientists due to its applicability in photonic band-gap and sensing materials. However, it is difficult to predict the behavior of the colloidal particles because it is highly dependent on the system. Slight change in the variables such as the temperature and pressure can change the phase from crystalline solid to amorphous liquid. The colloid particles are not only used for scientific purposes such as chemical and biological sensing [1-3] but are also interacting with us in our daily life. Some good examples are cosmetic products, food, and household goods [4-6]. Since we are interacting so much with these colloidal particles, it is critical for use to fully understand the behavior of these particles and their applications.

1.2 Colloidal Forces and Their Interactions

The colloidal particles provide a significant surface area to volume ratio which is why their interaction of their surfaces with each other becomes important when defining the final physical response of these suspensions. Such suspensions contain hydrodynamic, diffusive, gravitational and electrostatic forces. These forces can be dependent on the temperature, concentration, charge, size and shape of the particles which can give effect to the thickness of the colloidal structure (Figure 1.1 and Figure 1.2). The nature of these colloidal interactions defines the physical state of the suspension, which can vary from fully dispersed to an ordered assembly. In other words, the colloidal stability which refers to the ability of a suspension to resist aggregation defines the physical state of the suspension [7]. In order to promote the stability of the colloids, the influence

of the colloidal forces should be minimized. If there is no repulsive interaction between particles and the refractive index of the solvent and particles do not match, the dispersion will be unstable and aggregate into a colloidal gel [7]. In order to stabilize the colloidal suspension, the forces acting between the colloidal particles need to be modified. The different colloidal forces mentioned here can be quantified using the attractive and repulsive potentials shown below [8]:

$$V_{total}(h) = V_{vdW}(h) + V_{el}(h) + V_{dep}(h) \quad (1.1)$$

where $V_{total}(h)$ is the total inter-particle interaction energy, $V_{vdW}(h)$ is the attractive potential due to van der Waals force, $V_{el}(h)$ is the repulsive potential attributed to electrostatic force, and $V_{dep}(h)$ is the attractive or repulsive potential due to the presence of non-adsorbing species.[8] All of these factors vary as a function of h which is the separation distance.

The concentration of particles can also play a significant role in defining the structure. At low concentration and weak interaction, a dispersed phase can be observed. However, a balance of attractive and repulsive forces at sufficiently high concentrations, along with the entropy of the system, can lead to ordered phases [9, 10]. In addition, intermediate and high concentrations with large inter-particle interactions may lead to aggregated structures [11,12].

Another key feature of the colloids is their interaction through the excluded volume potential. The excluded volume potential for hard body is a short-range repulsive interaction, which prohibits interpenetration of particles. The value of this potential is infinite when the particles are in contact and zero when they are not in contact [13]. This hard body interactions

lead to disorder-order transitions at sufficiently high concentrations. Electrostatic and induced dipole moments give rise to repulsive or attractive forces that act on longer length scales than the excluded volume potential [14]. The electrostatic forces cause repulsive forces between the colloidal particles suspended in the ionic solution, where the ions in the solution adsorb onto the surface of the colloids and give it a net charge. By increasing the distance from the charged surface, the electrostatic potential decays exponentially. [13] On the other hand, the van der Waals forces cause attractive forces between the colloidal particles that occur from the interaction between fluctuating dipoles. The strength of the van der Waals force increases with the size of the particle, where the particle is composed of a large number of atoms or molecules.

The attractive forces favor aggregation of the particles. Large clusters of particles are seen in the suspension where the net force is an attractive force. The addition of non-adsorbing polymers (depletants) to the colloidal suspension can induce such attractive interactions. These depletants can be nanoparticles, polyelectrolytes, or polymers. [8] Also the addition of non-adsorbing polymers (depletants) can promote the overlapping of excluded volume of the colloidal particles which in result creates an unstable osmotic pressure. This unstable osmotic pressure increases the attractive force known as the depletion effect. When the strength is sufficient, the depletion potential can often lead to phase separation [15, 16].

1.3 Characterization of the Interactions Between Colloidal Particles

The phase behavior of the colloidal particles brought new possibilities to characterize interactions between colloidal particles. Methods for characterizing these interactions may vary considerably, but we can simply divide into techniques used for 2-D analysis and 3-D analysis. The traditional methods used to capture the interactions in the colloidal system includes colloidal

probe atomic force microscopy [17, 18], total internal reflection microscopy [19, 20], surface force apparatus [21, 22], and optical tweezers [23, 24]. These techniques perform 2-D analysis of particle interactions. These techniques perform 2-D analysis of particle interactions. Colloid probe atomic force microscopy, surface force apparatus, and the total internal reflection microscopy examine the interaction of a particle at the surface. This is important because the colloidal interactions for various surfaces can change the phase behavior of the system depending on the conditions. Optical tweezers is a technique to control the position of the particles by capturing them in optical traps. Because of these traps, it is possible to examine the particle-particle interactions.

Even though these techniques are very useful, they have their limitations. When the interest is focused on the particle-particle interactions, colloidal probe atomic force microscopy, surface force apparatus, and total internal reflection cannot provide the right information since these techniques are designed to capture the interactions of the particles on the surface. Also techniques that rely on systems that are refractive index mismatched for optical performances such as total internal reflection microscopy and optical tweezers would not work for colloidal systems that are dependent on solvents that have similar refractive indices.

These limitations have led to the development of new techniques in order to understand the particle-particle interactions better. Microscopy developments have allowed us to visualize the colloidal particles better. For example, confocal laser scanning microscopy is a technique that allows us to image deeper within a sample. Unlike optical microscopy, confocal laser scanning microscopy is unique because the scattering in the object plane is eliminated when the out-of-focus light is removed [25, 26].

Another great development that occurred in order to gain quantitative information from qualitative data is the development of image processing techniques. In the past, it was difficult to determine the particle position in the 3-D structure using a 2-D sliced image. With these image processing techniques developed by Crocker and Grier, now we can obtain the particle positions, radial distribution functions, and the mean free square displacement of the collective structures [27].

Then there is the simulation which is also beneficial in characterizing the colloidal particle interactions. Royall et al. showed how the pair potential could be constructed using simulations to take an experimentally determined radial distribution function and generating the effective pair interaction potential [28]. Lu et al. parameterized short-range attractive potentials of the micron-sized colloids by comparing the measurements of the second virial coefficient and the cluster mass distributions to the results of Monte Carlo (MC) simulations [29]. These developed simulation techniques demonstrates how the simulations and the experiments complement each other.

Still there is great interest in developing a direct pathway to characterize the colloidal interactions without going through the simulation process. A direct pathway that does not involve simulations would need quicker access to the potential allowing faster processing of the experimental data. The biggest challenge is to develop a pathway consistent with statistical mechanics that could be verified by the simulation data. Overcoming this challenge would greatly expand the possibilities to create a new methodology for experimentally capturing the interaction potential.

1.4 Self-Assembly of Colloidal Particles

1.4.1 Sedimentation

Self-assembly of colloidal particles is of great interest because of its various applications, such as photonic band-gap and sensing [30, 31]. With self-assembly, the behavior of colloidal particles can be naturally controlled. In other words, the particle behavior is dependent on the surrounding environment. Sedimentation operates under the influence of gravity as shown in Figure 1.4. A dilute suspension is typically created and the particles are settled at a particular sedimentation rate. This rate is defined by the density difference between the particles and the solvent. The magnitude of the difference decides how fast or slow the particles will settle. Sedimentation has been used to study a wide array of crystallization of colloidal particles [32-40]. It has been shown that high quality crystals can be achieved using this technique. The limitation of this technique is that the sedimentation typically takes on the order of days to weeks to achieve long-range ordered crystalline structures. This makes the sedimentation unfavorable for large-scale operations where the mass production is difficult.

There are many examples of sedimentation being used to form colloidal crystals. Davis demonstrated that hard-sphere crystallization of silica particles was possible under conditions where the initial volume fraction was dilute such that the crystallization rate was not impeded by the sedimentation rate [32, 33]. It is shown that the crystallization is controlled by the dimensionless Peclet number in addition to the initial volume fraction. Hoogenboom et al. provided a critical analysis of stacking faults in colloidal crystals. Also Leunissen et al. examined the sedimentation relating it to the binary colloidal crystallization [38, 41]. They proved that the crystallization is possible by controlling the charge on the particle and the size ratio between the

two particles. They also showed that it is possible to form not only the atomic analog cubic structures but also more complex structures such as LS6 and LS8 with long-range ordering.

The study of ionic colloidal crystals is of interest because of its limited work that has been done in this area. There is great potential in the application of this particular system, especially in photonics and photonic band-gap materials. Many of the studies focused on describing the conditions these ionic colloidal crystals will be stable and what structures will form. Less work has been done on understanding the kinetics behind ionic colloidal crystallization. More work should be focused on the mechanism of the colloidal crystallization.

1.4.2 Vertical Deposition

Vertical deposition a Langmuir-Blodgett like process was introduced by Colvin and his collaborators [42]. Figure 1.5 shows the schematic diagram of the vertical deposition setup. This method has gained great interest because of its simplicity. Also it does not require any special training and it is highly reproducible without generating major cracks. Much research has been done to identify the conditions which in result give good optical quality. It has been proved that for low solvent surface tension and low ionic strength, high substrate wettability, chemical or thermal modification of the particles, oscillatory motion in the meniscus and deposition on a tilted substrate, high crystalline quality has been observed [43-47]. When comparing with the sedimentation method, it has its unique advantage. If as suggested by Norris and his collaborators, the self-assembly at the air-liquid interface is a hydrodynamic phenomenon, then a greater flow of solvent through the forming crystals may generate better crystal quality [48]. However, when using the vertical deposition the possible structures that can be made are limited. For example, monodispersed colloidal systems tend to form a closed packed FCC structure [49].

Also the number of layers that can be deposit on the surface is limited compared to the sedimentation method.

Although there has been great work done focusing on the condition to generate good crystalline quality, still there are much more possible achievements that can be done in order to reproduce good quality crystalline structure for any material at any size colloids. Also as mentioned before, more interest is needed on the mechanism since there are numerous variables.

1.5 Fabrication of Colloidal-Crystal Thin Film

1.5.1 Fabrication of Two Dimensional Colloidal-Crystal Structure

There are two different types of two-dimensional structures; 2-D close-packed colloidal crystal structure and 2-D nonclose-packed colloidal crystal structure. The two-dimensional (2-D) close-packed colloidal crystals have been widely explored as sacrificial templates in creating arrays of nanopatterns [50]. In nanosphere lithography, a monolayer colloidal crystal or a double layer colloidal crystal (Figure 1.3 and Figure 1.7) are sometimes used to as a deposition or an etching mask in order to define the mosaic array of a microcolumnar structure [51]. The monolayer colloidal crystal mentioned here is a layer of spheres having a triangular pattern. This can be used to generate 2-D patterns on a substrate over a large scale. On the other hand, for double-layer colloidal crystals, the interstitials of the first layer partially overlap with those of the second layer. Using the combined interstitial as the template, patterns with different shapes and spatial arrangements can be fabricated [52]. There is also 2-D nonclosed packed colloidal crystal. Figure 1.6 shows a scanning electron microscope (SEM) image of a 2-D nonclosed packed colloidal crystal. This structure can be developed by using spin coating technique [53, 54].

Although these self-assembly approaches are favorable for laboratory-scale production, their scaling-up are problematic as they are not compatible with standard microfabrication techniques that have been widely used in microelectronic and photonic industries.

1.5.2 Fabrication of Three Dimensional Colloidal-Crystal Structure

Yablonovitch *et al.* was the first person to experimentally demonstrate the first 3-D photonic crystal in 1989. They built a relatively large 3-D structure designed to operate in the microwave region. This was because it was difficult to design small structures. From then many researchers focused on the fabrication of photonic crystals operating in the visible and near IR region. This effort gave rise to the methods that incorporates semiconductors and thin film technologies such as self-assembling colloids, optical methods, and electrochemical processes.

In this chapter I use the inverse opal structure to develop the basic structure. The process will be explained in more detail later in the Chapter 2. There are several approaches to make an inverse opal with a colloidal crystal as a template. Chemical vapor deposition (CVD), atomic layer deposition (ALD), sol-gel infilling, and electrodeposition are often used. CVD and ALD approach has been successful in filling colloidal crystal with dielectric materials, such as silicon, germanium, zinc oxide, titania, and even diamond [55-59]. However, due to the conformal growth pattern, the material does not completely fill the whole voids in the opal structure. For sol-gel infilling, dielectric materials [60] and metals [61] can be used. Unfortunately, the shrinkage during the drying process or heat treatment is a major problem when dealing with sol-gel methods. As a result, multiple coating steps are usually required. [62] Electrodeposition is also a common but a unique method for some reasons. First, the material is infilled into the interstitial space and does not exit the pores. Also since the electrodeposition starts from the substrate, the thickness of the inverse opal can be controlled by the plating charge, which is

independent from the thickness of colloidal template to start with. Lastly, it is very easy to form layered composite inverse opal or embed a layer of functional defect into the inverse opal by simply switch to a different plating solution. However electroplating has its own disadvantages. Electroplating only works with materials that are electrically conductive. As a result, this approach has been limited to metals [63], semiconductors [64] and conductive polymers [65] (Figure 1.9).

1.6 Sintering

The sintering process allows the opals to have mechanical stability and connects every sphere with its neighbors. The fabrication of the inverse opal strongly depends on the connectivity between particles provided by the sintering process. Sintering also permits to control the opal void volume, a crucial parameter in the search for optimal semiconductor infilling and, therefore, the maximum gap width (Figure 1.10, Table 1.1). Figure 1.8 represents the scanning electron microscope (SEM) image of the cracked structure and the crack free structure.

1.7 Tables

Table 1. Summary of Data for Particles after the Indicated Treatment

material	refractive index ^a ($\lambda = 589$ nm)	colloid diameter	predicted Bragg peak	observed Bragg peak
as-made	1.44–1.46	205–215 nm	448–473 nm	454 nm (broad)
calcined	1.439	193 nm	422 nm	425 nm
sintered	1.457	188 nm	415 nm	414 nm
rehydroxylated	1.457			409 nm

Table 1.1. The summary of Data for Particles after the Indicated Treatment [69].

1.8 Figures

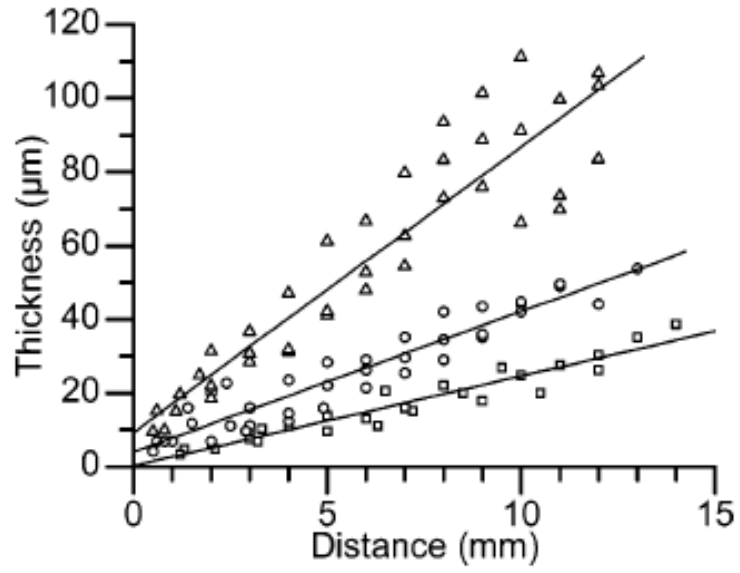


Figure 1.1. The thickness profiles of the colloidal crystals deposited at $\phi = 0.2\%$ (squares), 0.4% (circles), and 0.8% (triangles) [66].

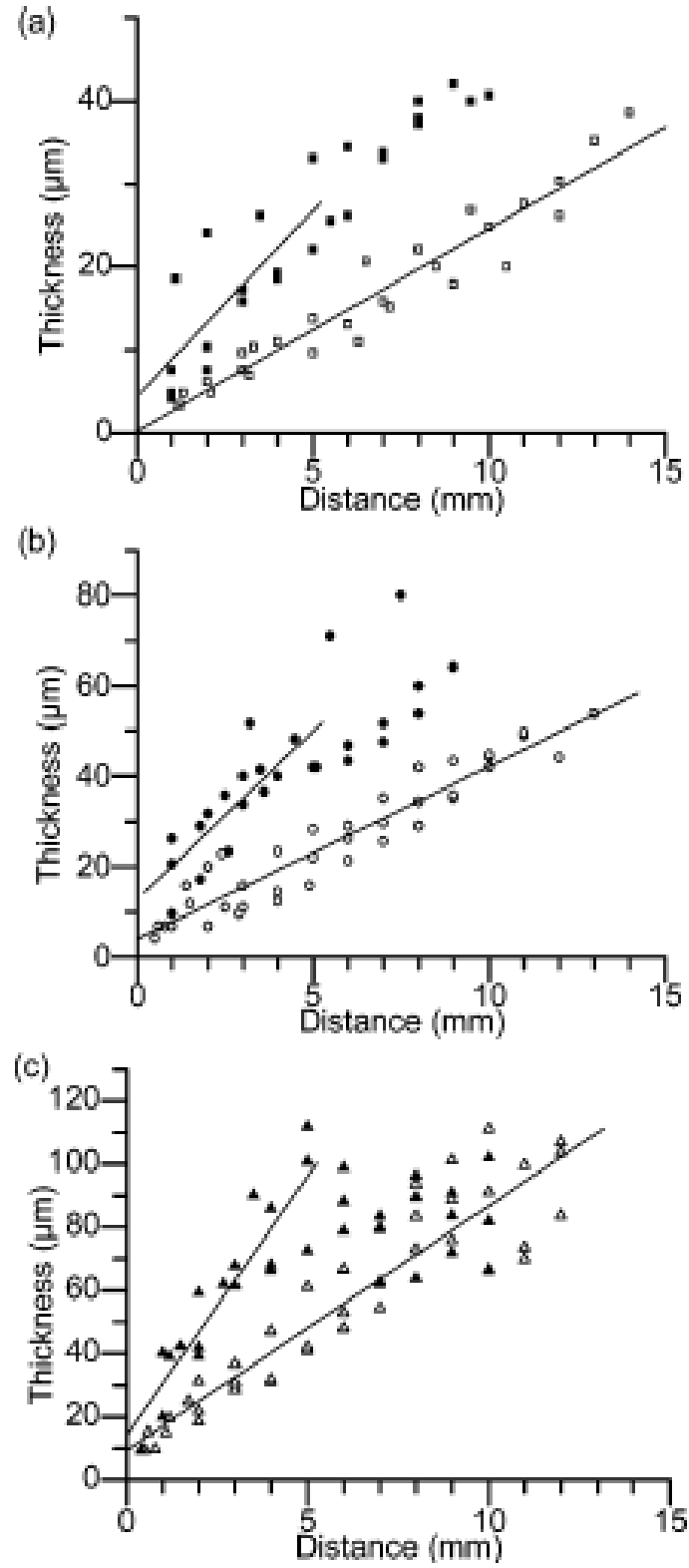


Figure 1.2. The comparison of thickness profiles of colloidal crystals deposited with and without solvent infusion at $\phi =$ (a) 0.2%, (b) 0.4%, and (c) 0.8% [66].

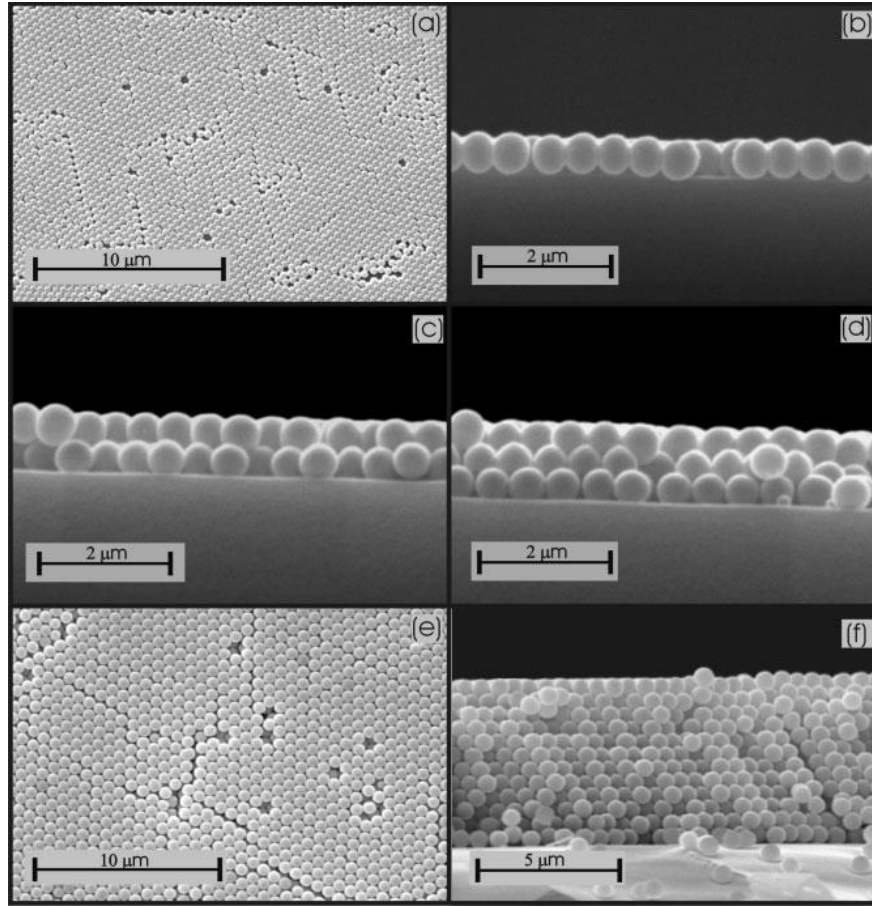


Figure 1.3. The SEM images of spin-coated, [111]-oriented colloidal crystals built from dispersions containing a–d) 30% silica particles (440 nm diameter) in a mixture of ethanol and EG (35 vol% each) and e,f) 50% silica spheres (600 nm diameter) in a mixture of water (10 vol %) and EG (40 vol %) at various spinning velocities. a) Top view of a monolayer of silica spheres packed hexagonally, obtained at $\omega = 175$ rps. We also show side views of b) the previously mentioned monolayer, c) a bilayer obtained at $\omega = 125$ rps, and d) a 3 ML stacking of silica spheres produced at $\omega = 75$ rps. Images in (e) and (f) are top and side views of 12 ML fcc photonic colloidal crystal grown at $\omega = 25$ rps [67].

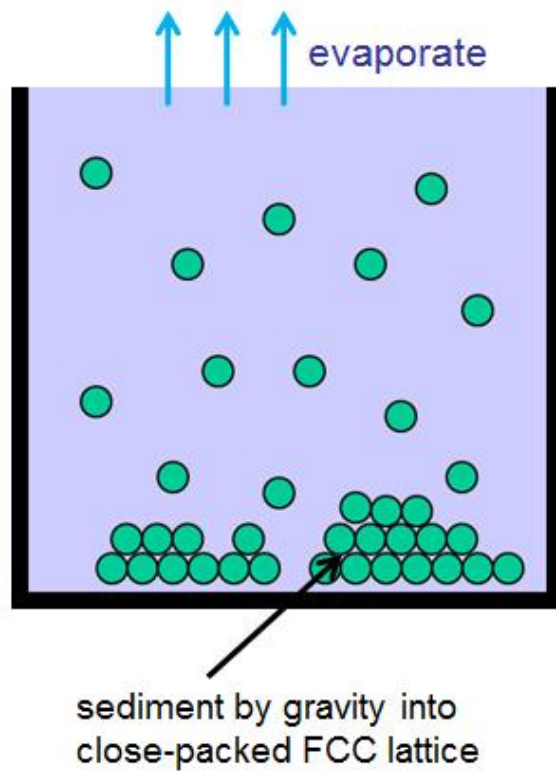


Figure 1.4. The schematic diagram of the sedimentation setup.

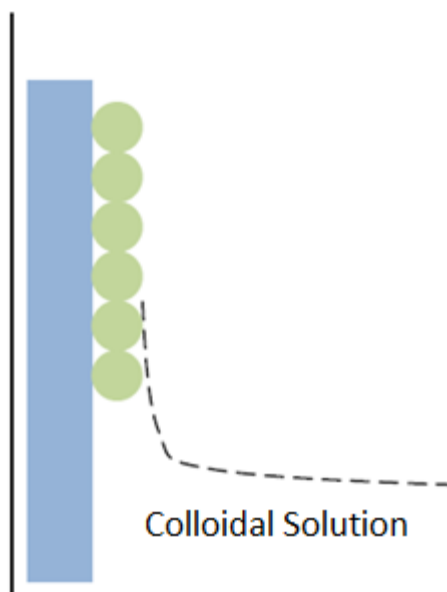


Figure 1.5. The schematic diagram of the vertical deposition setup.

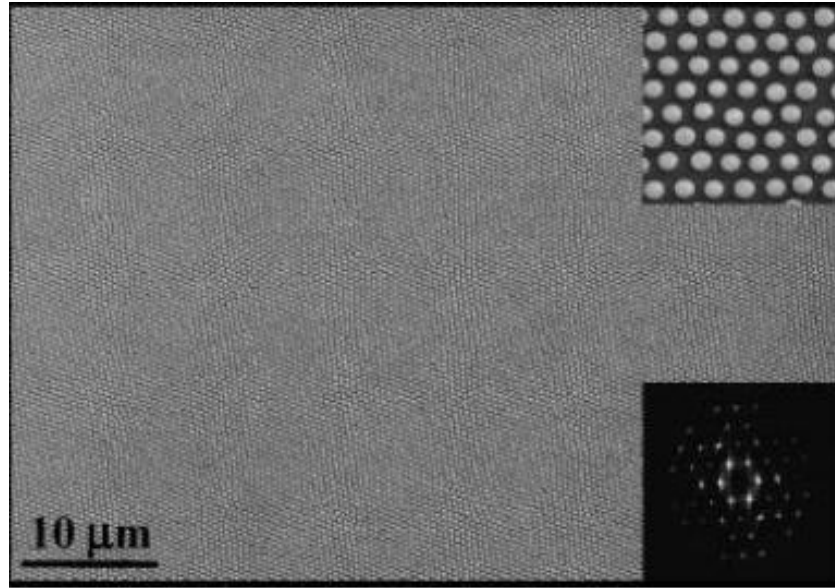


Figure 1.6. The SEM image of a 2-D nonclose packed silica colloidal crystal. The upper inset showing a higher-magnification image and the bottom inset showing a Fourier transform of a $40\ \mu\text{m} \times 40\ \mu\text{m}$ region.

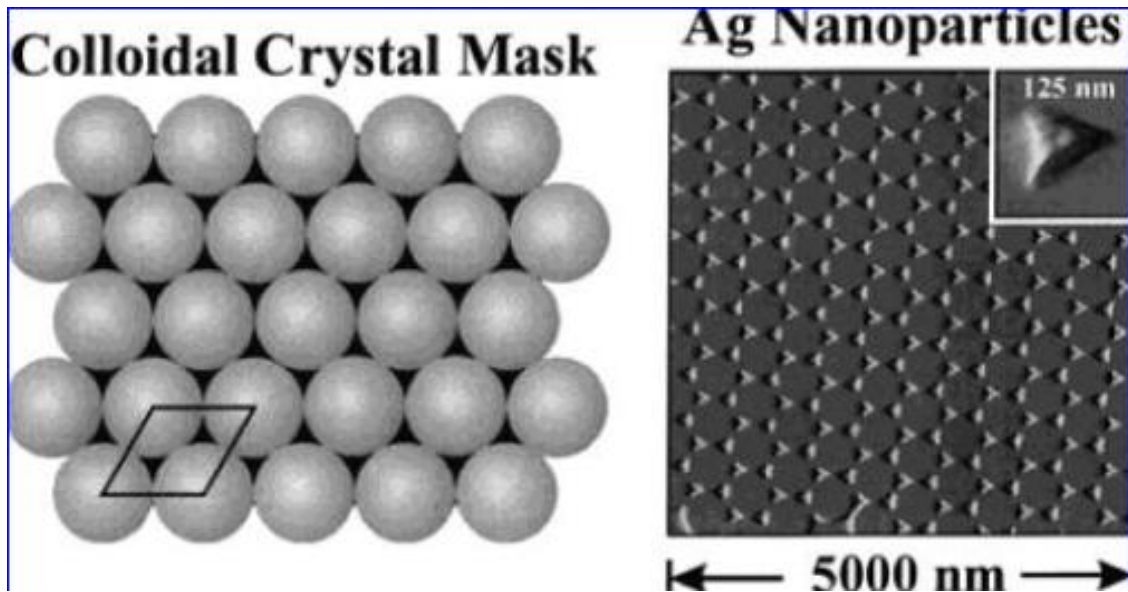


Figure 1.7. The colloidal monolayer mask and silver nanoparticle array formed by directionally depositing silver through the mask. Figures adopted from reference [52].

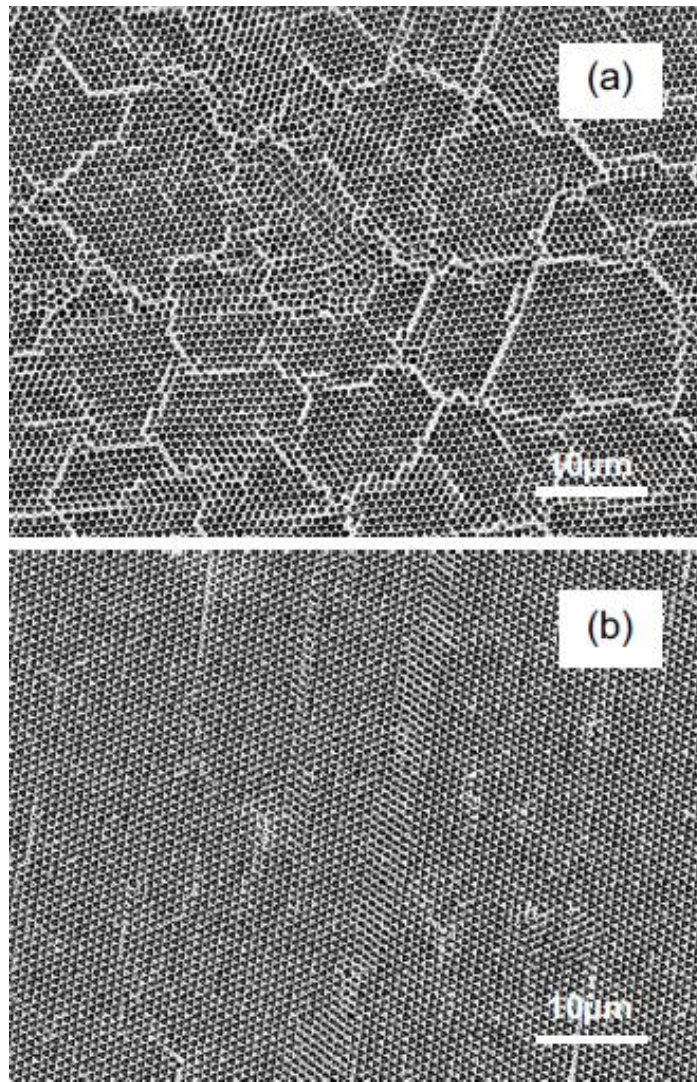


Figure 1.8. (a) The SEM image of a heavily-cracked Si inverted opal. The opal template for the crystal was assembled of 850 nm silica spheres; the cracks appeared during Si LPCVD due to shrinkage of the spheres. (b) The SEM image of a crack-free Si inverted opal. The spheres were sintered as a dry powder at 6000C for 4 hours prior to assembly of the opal; after the heat treatment, the diameter of the spheres was 792 nm [68].

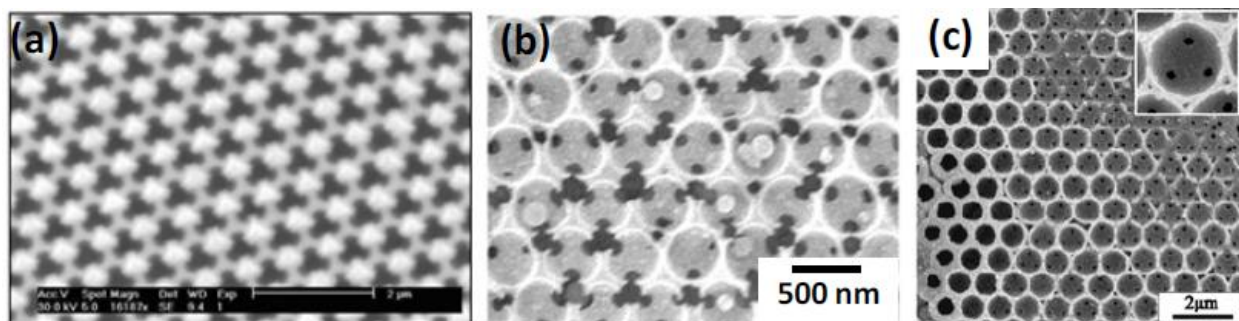


Figure 1.9. The SEM images of the electrodeposited inverse opal made of (a) platinum [63], (b) GaAs [64], and (c) poly (pyrrole) [65]

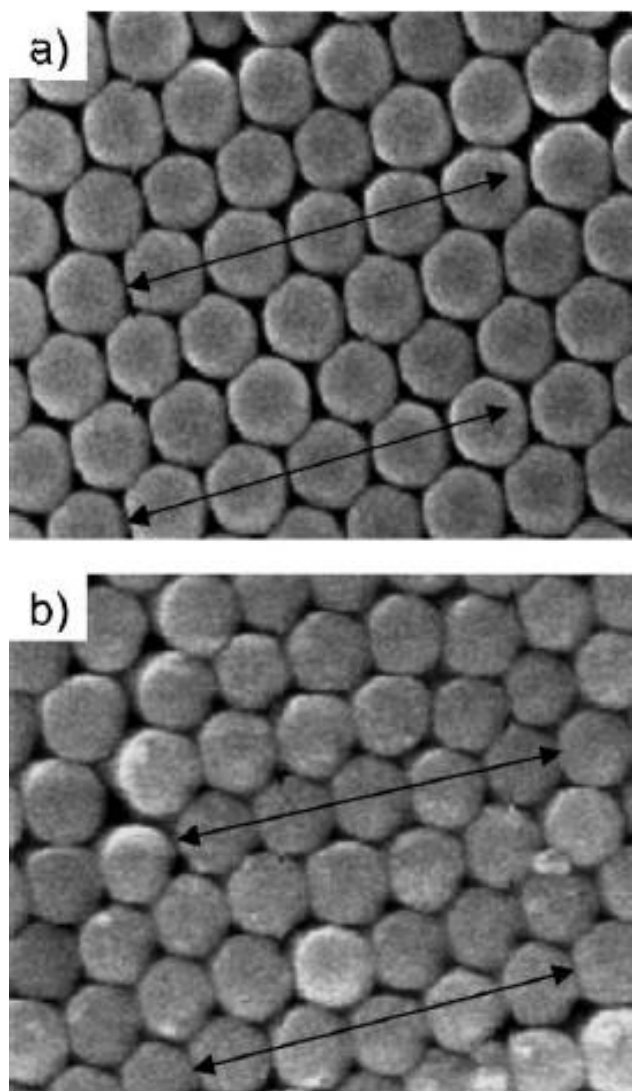


Figure 1.10. The SEM images of colloidal crystal made from a) as-made particles, and b) calcined particles. The arrow size is the same in each panel to indicate that the particles in panel b are smaller. [69]

1.9 References

1. Whitesides, G. M.; Boncheva, M. *Proceedings of the National Academy of Sciences of the United States of America* **2002**, 99, (8), 4769-4774.
2. Horsch, M. A.; Zhang, Z.; Glotzer, S. C. *Nano Letters* **2006**, 6, 2406-2413.
3. van Kats, C. M.; Johnson, P. M.; van den Meerakker, J.; van Blaaderen, A. *Langmuir* **2004**, 20, (25), 11201-11207.
4. Cush, R.; Dorman, D.; Russo, P. S. *Macromolecules* **2004**, 37, (25), 9577-9584.
5. Hong, L.; Anthony, S. M.; Granick, S. *Langmuir* **2006**, 22, (17), 7128-7131.
6. Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. *A. Science* **2002**, 298, (5595), 1006-1009.
7. Hiemenz, P.C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*. Third ed. Marcel Dekker, Inc., New York 1997.
8. Tohver, V. *Phase Behavior, Structure, and Properties of Colloidal Microsphere-Nanoparticle Mixtures*; University of Illinois: Urbana, IL, 2001.
9. Hynninen, A. P.; Leunissen, M. E.; van Blaaderen, A.; Dijkstra, M. *Physical Review Letters* **2006**, 96, (1), 4.
10. Onsager, L. *Annals of the New York Academy of Sciences* **1949**, 51, (4), 627-659.
11. Sanz, E.; Leunissen, M. E.; Fortini, A.; van Blaaderen, A.; Dijkstra, M. *Journal of Physical Chemistry B* **2008**, 112, (35), 10861-10872.
12. Valverde, J. M.; Quintanilla, M. A. S.; Castellanos, A. *Physical Review Letters* **2004**, 92, (25).
13. Tretiakov, K. V.; Wojciechowski, K. W. *Physica Status Solidi B-Basic Solid State Physics* **2005**, 242, (3), 730-741.

14. Larson, R.G. The Structure and Rheology of Complex Fluids, *Oxford University Press*, *Oxford* **1999**.
15. Asakura, S.; Oosawa, F. *Journal of Chemical Physics* **1954**, 22, (7), 1255-1256.
16. Asakura, S.; Oosawa, F. *Journal of Polymer Science* **1958**, 33, (126), 183-192.
17. McKee, C. T.; Clark, S. C.; Walz, J. Y.; Ducker, W. A. *Langmuir*, **2005**. 21, (13), 5783-5789.
18. Butt, H. J.; Cappella, B.; Kappl, M. *Surface Science Reports*, **2005**. 59, (1-6), 1-152.
19. Israelachvili, J.N., *Intermolecular and surface forces*. 2nd ed. **1992**, London: Academic. xxi, 450 p.
20. Schorr, P. A.; Kwan, T. C. B.; Kilbey, S. M.; Shaqfeh, E. S. G.; Tirrell, M. *Macromolecules*, **2003**. 36, (2), 389-398.
21. Bevan, M. A.; Prieve, D. C. *Langmuir*, **1999**. 15, (23), 7925-7936.
22. Claesson, P.M.; Ederth, T.; Bergeron, V.; Rutland, M. W. *Advances in Colloid and Interface Science*, **1996**. 67, 119-183.
23. Furst, E. M. *Soft Materials*, **2003**. 1, (2), 167-185.
24. Sainis, S. K.; Germain, V.; Mejean, C. O.; Dufresne, E. R. *Langmuir*, **2008**. 24, (4), 1160-1164.
25. Pawley, J. B., *Handbook of biological confocal microscopy*. 2nd ed. **1995**, New York: Plenum Press. xxiii, 632 p.
26. Solomon, M. J.; Kogan, M., *Encyclopedia of Condensed Matter Physics*, **2005**, 229-235.
27. Crocker, J.C.; Grier, D.G. *Journal of Colloid and Interface Science*, **1996**. 179, (1), 298-310.

28. Royall, C. P.; Louis, A. A.; Tanaka, H. *Journal of Chemical Physics*, **2007**. 127, (4), 044507.
29. Lu, P. J.; Zaccarelli, E.; Ciulla, F.; Schofield, A. B.; Sciortino, F.; Weitz, D. A. *Nature*, **2008**. 453, (7194), 499-U4.
30. Ngo, T. T.; Liddell, C. M.; Ghebrebrhan, M.; Joannopoulos, J. D. *Applied Physics Letters*, **2006**. 88, (24), 241920.
31. Hosein, I. D.; Liddell, C. M. *Langmuir*, **2007**. 23, (21), 10479-10485.
32. Davis, K. E.; Russel, W. B.; Glantschnig, W. J. *Journal of the Chemical Society-Faraday Transactions*, **1991**. 87, (3), 411-424.
33. Davis, K. E.; Russel, W. B.; Glantschnig, W. J. *Science*, **1989**. 245, (4917), 507-510.
34. Leunissen, M.E.; Sullivan, M.T.; Chaikin, P.M.; van Blaaderen, A. *Journal of Chemical Physics*, **2008**. 128, (16).
35. Ackerson, B.J.; Paulin, S.E.; Johnson, B.; van Megen, W.; Underwood, S. *Physical Review E*, **1999**. 59, (6), 6903-6913.
36. Shereda, L.T.; Larson, R.G.; Solomon, M.J. *Physical Review Letters*, **2008**. 101, (3).
37. Royall, C.P.; van Roij, R.; van Blaaderen, A. *Journal of Physics-Condensed Matter*, **2005**. 17, (15), 2315-2326. 12.
38. Leunissen, M.E.; Christova, C.G.; Hynninen, A.P.; Royall, C.P.; Campbell, A.I.; Imhof, A.; Dijkstra, M.; van Roij, R.; van Blaaderen, A. *Nature*, **2005**. 437, (7056), 235-240.
39. Vermolen, E.C.M.; Kuijk, A.; Fillion, L.C.; Hermes, M.; Thijssen, J.H.J.; Dijkstra, M.; van Blaaderen, A. *Proceedings of the National Academy of Sciences of the United States of America*, **2009**. 106, (38), 16063-16067.

40. Hilhorst, J.; Abramova, V.V.; Sinitskii, A.; Sapoletova, N.A.; Napolskii, K.S.; Eliseev, A.A.; Byelov, D.V.; Grigoryeva, N.A.; Vasilieva, A.V.; Bouwman, W.G.; Kvashnina, K.; Snigirev, A.; Grigoriev, S.V.; Petukhov, A.V. *Langmuir*, **2009**, 25, (17), 10408-10412.
41. Hoogenboom, J.P.; Derks, D.; Vergeer, P.; van Blaaderen, A. *Journal of Chemical Physics*, **2002**, 117, (24), 11320-11328.
42. Jiang P.; Bertone J. F; Hwang K. S.; Colvin V. L. *Chem. Mater.* **1999**, 11, 2132–2140
43. Cortalezzi, M. M.; Colvin, V.; Wiesner, M. R. *J. Colloid Interface Sci.* **2005**, 283, 366-372.
44. Teh, L. K.; Tan, N. K.; Wong, C. C.; Li, S. *Appl. Phys. A* **2005**, 81, 1399-1404.
45. Goldenberg, L. M.; Jung, B.-D.; Wagner, J.; Stumpe, J.; Paulke, B.-R.; Görnitz, E. *Langmuir* **2003**, 205-207.
46. Cademartiri, L.; Sutti, A.; Calestani, G.; Dionigi, C.; Nozar, P.; Migliori, A. *Langmuir* **2003**, 19, 7944-7947.
47. Im, S. H.; Kim, M. H.; Park, O. O. *Chem. Mater.* **2003**, 15, 1797-1802.
48. Norris, D. J.; Arlinghaus, E. G.; Meng, L.; Heiny, R.; Scriven, L. E. *Adv. Mater.* **2004**, 16, 1393-1399.
49. McLachlan, M. A.; Johnson, N. P.; De La Rue, R. M.; McComb, D. W. *J. Mater. Chem.* **2004**, 14, 144-150.
50. McLellan, J. M.; Geissler, M.; Xia, Y. N. *J. Am. Chem. Soc.* **2004**, 126, 10830-10831.
51. Deckman, H. W.; Dunsmuir, J. H. *Appl. Phys. Lett.* **1982**, 41, 377- 379.
52. Haynes, C. L.; Van Duyne, R. P. *Journal of Physical Chemistry B* **2001**, 105, (24), 5599-5611.
53. Jiang, P.; McFarland, M. J. *J. Am. Chem. Soc.* **2004**, 126, 13778-13786.

54. Jiang, P.; Prasad, T.; McFarland, M. J.; Colvin, V. L. Manuscript in preparation.
55. Vlasov, Y. A.; Bo, X. Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, 414, (6861), 289-293.
56. Miguez, H.; Chomski, E.; Garcia-Santamaria, F.; Ibisate, M.; John, S.; Lopez, C.; Meseguer, F.; Mondia, J. P.; Ozin, G. A.; Toader, O.; van Driel, H. M. *Advanced Materials* **2001**, 13, (21), 1634-+.
57. Juarez, B. H.; Garcia, P. D.; Golmayo, D.; Blanco, A.; Lopez, C. *Advanced Materials* **2005**, 17, (22), 2761-+. 16.
58. King, J. S.; Heineman, D.; Graugnard, E.; Summers, C. J. *Applied Surface Science* **2005**, 244, (1-4), 511-516.
59. Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C. X.; Khayrullin, I.; Dantas, S. O.; Marti, I.; Ralchenko, V. G. *Science* **1998**, 282, (5390), 897-901.
60. Zhang, X. B.; Guo, C. C.; Li, Z. Z.; Shen, G. L.; Yu, R. Q. *Analytical Chemistry* **2002**, 74, (4), 821-825.
61. Denny, N. R.; Han, S. E.; Norris, D. J.; Stein, A. *Chemistry of Materials* **2007**, 19, 4563-4569.
62. Jiang, P.; Bertone, J. F.; Colvin, V. L. *Science* **2001**, 291, (5503), 453-457.
63. Bartlett, P. N.; Baumberg, J. J.; Coyle, S.; Abdelsalam, M. E. *Faraday Discussions* **2004**, 125, 117-132.
64. Lee, Y. C.; Kuo, T. J.; Hsu, C. J.; Su, Y. W.; Chen, C. C. *Langmuir* **2002**, 18, (25), 9942-9946.
65. Cassagneau, T.; Caruso, F. *Advanced Materials* **2002**, 14, (1), 34-38.
66. Shimmin, R. G.; DiMauro, J.; Braun, P. V. *Langmuir* **2006**, 22, 6507-6513

67. Mihi, A.; Ocana, M.; Miguez, H. *Advanced Materials* **2006**, 18, (17), 2244-2249, 0935-9648.
68. Chabanov, A. A.; Jun, Y.; Norris, D. J. *Applied Physics Letters* **2004**, 84, (18), 3573-3575.
69. Van Le, T.; Ross, E. E.; Velarde, T. R. C.; Legg, M. A.; Wirth, M. J. *Langmuir* **2007**, 23, 8554-8559.
70. Barton, J. E.; Odom, T. W. *Nano Lett.* **2004**, 4, 1525-1528.
71. Choi, D. G.; Yu, H. K.; Jang, S. G.; Yang, S. M. *J. Am. Chem. Soc.* **2004**, 126, 7019-7025.
72. Choi, D. G.; Kim, S.; Jang, S. G.; Yang, S. M.; Jeong, J. R.; Shin, S. C. *Chem. Mater.* **2004**, 16, 4208- 4211.
73. Jiang, P. *Angew. Chem., Int. Ed.* **2004**, 43, 5625-5628. (f) Hakanson, U.; Persson, J.; Persson, F.; Svensson, H.; Montelius, L.; Johansson, M. K. J. *Nanotechnology* **2003**, 14, 675-679.
74. Lu, Y.; Xiong, H.; Jiang X.; Xia, Y. N.; Prentiss, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, 125, 12724-12725.

CHAPTER 2

Micromechanical Devices Having 3-D Inverse Opal Microstructure

2.1 Introduction

Materials with three-dimensional (3-D) micro structure are of great interest for their optical [1-4], acoustic [5, 6], thermal [7, 8], and mechanical properties [9-11]. A few microelectromechanical system (MEMS) devices have been fabricated from micro structured materials. However, generally these devices have been limited to 2-D structures [12-15] where much research has been done. For example, 2-D nanostructure array at the free end of a micro cantilever enabled Raman resonance during atomic force microscopy [13]. Another example is a micro cantilever having an array of through-thickness nanochannels of size 40 nm, which created a high surface to volume ratio required for chemical sensing [14]. However, as mentioned before, published research on MEMS devices using photonic crystal materials has been limited to 2-D structures with little work done on the integration of regular 3-D microstructures into MEMS devices to take advantage of either the optical or mechanical properties of a 3-D micro structured device. In this chapter we demonstrated the fabrication and mechanical properties of highly porous micromechanical devices containing an internal 3-D inverse opal microstructure. Also there is even potential to fabricate composite cantilevers with various materials that have very different mechanical properties.

In this chapter, we introduce two MEMS devices fabricated with internal 3-D microstructures. The first device is a micro cantilevers with 3-D nickel inverse opal microstructure and the other is an alumina shell microstructure. The volume fraction metal of the microcantilevers containing 3-D nickel inverse opal microstructure can be tuned from 6% to 80% by controlling the electroplating recipe or performing electropolishing.

Also using these porous microcantilevers as templates, we then deposited a thin layer of alumina onto the nickel microstructure before sacrificing the nickel, resulting in a microcantilever consisting of a novel periodic alumina shell structure with an alumina volume fraction as low as 1%.

2.2 Nickel Inverse Opal Cantilevers

2.2.1 The Preparation of Conductive Substrate

The fabrication of the conductive substrate starts with a 4 inch double-sided polished silicon wafer having a layer of 300 nm thick thermal oxide. A thin layer of gold film (~50 nm) is then evaporated on to the wafer with a chromium adhesive layer (1~5 nm) and then patterned to the microcantilever geometry (Figure 2.1). After the micro cantilever is cut into 1 cm by 3 cm chips, the substrate is then cleaned in piranha solution (3:1 mixture of sulfuric acid and 30% hydrogen peroxide) at ~100 °C for 4 hours, followed by rinsing with deionized (DI) water and blow drying with N₂. The substrates are then soaked in 10mM 3-Mercapto-1-propanesulfonic acid, sodium salt (HS-(CH₂)₃-SO₃Na) aqueous solution for 2 hours on order to form a monolayer of negatively charged molecules on the gold surface. After rinsing again with deionized (DI) water and drying with N₂, the substrates are ready to use. If other metal such as tungsten is used instead of gold, where the native oxide provides a high enough surface charge density, the step of self-assembled monolayer treatment can be skipped.

2.2.2 Colloidal Crystal Growth on Conductive Substrate

After the conductive substrate is prepared, the next step is growing colloidal crystals on the substrate through self-assembly. Self-assembly technique has been extensively studied over the years, which in result forms a face-centered cubic lattice structure [16, 17]. For this

experiment vertical deposition process is used. Also sulfate terminated polystyrene particles are used due to the charge of the colloids. The charge of the colloids needs to be the same as the SAM layer in order to avoid colloids from randomly pack. The diameter of the polystyrene particles can range from 500 nm to 2.8 μm ; in this experiment we mainly use 1.8 μm because of their monodispersity and high surface charge to achieve high quality opal structure.

2.2.3 Electrodeposition

The polystyrene colloidal particles that are grown on the substrate are held together by a weak Van der Waals force, which is too weak to survive when going through the electrodeposition step. In order to improve this weak force, the colloidal crystals are sintered at temperatures slightly lower than the glass transition temperature of polystyrene, which is around 95 °C. This sintering process allows the particles to deform in a slowly and controllably. Also the time of the sintering is very important. Normally 2~5 hours are acceptable. Even though the interconnection between the particles may get stronger, over sintering will allow the whole film to detach from the substrate due to massive lateral shrinkage. Even though various metal such Au, Ag W, Pt, Pd, Co, Ni and Zn can be used to form inverse opals, nickel is selected in this experiment because of its high reflectivity in the infra-red, temperature stability, and ease of electrochemical processing. The thickness of the nickel film can be regulated by controlling the total charge passed during deposition. After the electrodeposition, the PS particles are then removed using tetrahydrofuran (THF), resulting in a 3-D nickel inverse opal (Figure 2.2). Although the electrodeposition is quite homogeneous, the gradual thickness variations may occur over the sample surface.

After several layers of polystyrene opals are grown on the gold surface, nickel is grown using nickel electroplating. The cantilever release process is the same as the release process of silicon heated cantilevers (Figure 2.1) [18]. Figure 2.3 is the scanning electron microscope (SEM) images of a released 3D nickel inverse opal microstructured cantilever. It is shown in Figure 2.3a that the monodispersed 3D inverse opal porosity extends through the cantilever in all three dimensions. Figure 2.4a and Figure 2.4b shows the top surface of the two microcantilevers with nickel volume fractions of 0.22 and 0.15. It has been shown that the nickel volume fraction can be reduced to under 6% before the structure falls apart [16].

Also inverse opal cantilevers containing multiple layers of various metals can be fabricated through multiple electroplating steps. Figure 2.4c shows the cross-section of a microcantilever made of two metals. The gold layer is deposited first and then the nickel layer is deposited. The boundary of the gold nickel layer is marked with a white dashed line. However, when observing the image, the nickel layer is more porous compared to the gold layer. This is because the micro cantilever was immersed in nickel etching solution and pulse etched shortly. This shows that we can selectively decrease the metal volume fraction by using the proper etching solution and proper time. The fabrication process is the same as the fabrication process for the cantilevers with a nickel inverse opal microstructure except with a different pattern of gold seed layer and an extra step of metal electroplating.

2.3 Al₂O₃ Microcantilevers

One important application for cantilever based devices is chemical/mass sensing. For our research, it is desirable to have a cantilever with a volume fraction as small as possible, while keeping the surface area as large as possible. The minimum volume fraction of a cantilever with

a 3-D nickel inverse opal microstructure is around 6%. To make the volume fraction even smaller, we developed a new microcantilever with a shell microstructure. Here the microfabrication process of a cantilever with a shell structure is shown from Figure 2.5a to Figure 2.5c. We start by a cantilever with a nickel inverse opal structure. We then deposit 75 nm of alumina through atomic layer deposition (ALD). ALD is used because ALD can deposit alumina film uniformly not only on the outside of the cantilever, but also in the entire inner surfaces. Next, a focus ion beam (FIB) is used to cut off the cantilever's edges to expose the nickel. The cantilever is then soaked in nickel etchant until only the alumina shell remains. Figure 2.5d to Figure 2.5f shows SEM images of a cantilever with alumina shell structure and magnified images of its cross-section. Figure 2.6a to Figure 2.6c shows the optical images of a cantilever during the nickel etching process. This cantilever only has the end edge cut off. Because the alumina film protects the structure, the nickel structure is only etched in the Y direction. Figure 2.6d shows an optical image of a cantilever with all the nickel etched away. The volume fraction of cantilevers with an alumina shell structure can go down to 1% by depositing thinner alumina layer. Other than making cantilevers with alumina shell structure, the same method can be applied to make shell structures with other materials only if the material can be deposited conformally through ALD and is not etched by the nickel etchant.

2.4 The Mechanical Properties of 3-Dimensional Nickel Inverse Opal Cantilevers

It is known that soft cantilevers with high resonant frequencies are desired for biological samples [19]. This can be easily achieved by fabricating the cantilevers with lower mass. Usually the traditional approach is to make the cantilever smaller. However, by making the cantilever with 3-D inverse opal microstructure, the same goal can be achieved by lowering the volume fraction of the cantilever microstructure. For example, when a cantilever is made of nickel

inverse opal microstructure with volume fraction 0.15 instead of solid nickel, the spring constant is approximately 12 times smaller while the resonant frequency is only about 1.34 times smaller.

In this chapter the mechanical properties of solid silicon, solid nickel, nickel inverse opal microstructure and alumina shell microstructure were measured with AFM (Asylum MFP3D) and Agilent Nanoindenter (MT200). In order to determine the resonant frequency of a cantilever, thermal spectrum of the cantilever was measured in an AFM. A typical measurement is shown in Figure 2.7a and the magnified fundamental resonant frequency peak is shown in the inset of Figure 2.7a. By fitting the fundamental resonance peak in the software, the quality factor of the cantilever can be determined. Besides resonant frequency and quality factor, an AFM is also used to measure the spring constant of the soft cantilevers (smaller than 1 N/m). This is done by measuring the force distance curve and resonant frequency of the soft cantilevers. For relative stiff cantilevers, the spring constant was measured in the Nanoindenter. In these measurements, the cantilevers were deflected at different positions by the Nanoindenter from the end of the cantilevers. The load curves are linear with displacement and the slope of these curves are the spring constant of the cantilever with the corresponding effective length. By fitting these spring constants with a theoretical model where k is proportional to $1/L^3$, we can obtain the spring constant of the cantilever. With the spring constant obtained and the dimension of the cantilever, the effective Young's modulus of the nickel inverse opal structure was calculated by plugging into the equation below:

$$E=4kL^3/Wt^3 \quad (1)$$

where k is the spring constant, L , W and t are the length, width and thickness of the cantilever. Figure 2.7b shows the measured effective Young's modulus of 3-D nickel inverse opal

microstructures with different volume fractions. Also, Table 2.1 shows more detail mechanical measurement results for cantilevers made of different materials and different volume fraction. Figure 2.9 shows the spring constant measurement of a cantilever with a 3-D nickel inverse opal microstructure in an Agilent Nanoindenter (Figure 2.8). Figure 2.9a shows the measured load and displacement curves when the cantilever is deflected at different positions from the end of the cantilever. The load curves are linear with displacement and the slope of these curves is the spring constants of the cantilever with the corresponding effective length. Figure 2.9b shows the measured spring constants with different effective lengths. By fitting these measurements with a theoretical model (k is proportional to $1/L^3$), we can find the spring constant of the cantilever.

2.5 Conclusion

We have not only fabricated MEMS devices having an inverse opal structure but also demonstrated that high quality metallic photonic crystal structures can be made through a combination of colloidal crystal templating and electrodeposition (Figure 2.3 and Figure 2.10). Also, we were able to form the inverse opal structure on any mixed pattern shown in Figure 2.11. These devices have tunable volume fraction with a regular lattice microstructure which is shown in Figure 2.4. The volume fraction can be tuned from 6% to 80% for microcantilevers with a 3-D nickel inverse opal microstructure and it can be as low as 1% for microcantilevers with an alumina shell structure which is shown in Figure 2.5 and Figure 2.6. Table 2.1 summarizes the mechanical properties of similar MEMS devices with materials and volume fractions.

2.6 Experimental

In order to fabricate a 3-D nickel inverse opal microstructure cantilever we start with a 4 inch double-sided polished silicon wafer. After sputtering 10 nm of chromium and 50 nm of gold, a thin layer of photoresist (Shipley 1827) is spun on it at 3000 rpm for 40 sec. The wafer is then

exposed in a mask aligner (EV420) for 20 sec and developed in photoresist developer (MF319) for 80 sec. After baking the wafer in the oven at 110°C for 10 min, the gold layer is etched using the gold etchant (Transene, type TFA) for 25 sec and chromium etchant (HTA Enterprise, CEP-200) for 20 sec. The wafer is soaked in acetone for 10 min followed by 10 min oxygen plasma clean in order to remove the photo resist. Finally the wafer is cut into 1 cm by 3 cm chips for the next step.

The process of developing the nickel inverse opal structure starts by a Piranha cleaning process in order to remove any impurities attached on the surface. This is done by first making a mixed solution of sulfuric acid and hydrogen peroxide in the ratio of 3:1. The total volume of the mixed solution does not matter unless the mixing ratio is consistent we heat the cantilever chip into this solution at 100 °C for 4 hours. The cantilever chip is then rinsed with DI water and immersed in a saturated 3-mercaptopropylsulfonic acid, sodium salt ($\text{HS}-(\text{CH}_2)_3-\text{SO}_3\text{Na}$) water based solution for 2 hours forming a monolayer of hydrophilic molecules on the gold surface. 1.8 μm diameter sulfate terminated polystyrene spheres (Molecular Probes Inc.) are formed into an opal film on conductive substrate through evaporative deposition at 55 °C with a colloid volume concentration of 0.4% in water [20]. Ni was then electrodeposited using electro deposition solution Techni Nickel S (Technic) under constant current mode ($1 \text{ mA}/\text{cm}^2$) in a two-electrode setup with using with a platinum flag foil as the anode. Finally the PS opal is removed by immersing the sample in tetrahydrofuran (THF) for 2 hours.

To separate the cantilever with the nickel inverse opal microstructure, we spin both sides of the chip with an adhesion layer (AP 8000) at 3000 rpm and a thick photoresist layer (AZ 4620) at 1000 rpm for 40 sec. The back side of the chip is then exposed under the mask aligner for 25 sec and developed in photoresist developer (AZ400k, 1:2 in DI water) for 90 sec. After

baking the chip on the hotplate at 110°C for 10 min, we attach the chip to a carrier wafer with freshly spun photoresist (AZ 4620, 1000 rpm). The carrier wafer with the chip attached is then baked again at 110 °C for 10 min and 130 °C for another 10 min. The silicon substrate is etched through in a PlasmaTherm ICP with the Bosch process. The chip and the carrier wafer are separated by soaking in photoresist stripper (AZ400T) at 70 °C for 4 hours. Last, the chip is dip into 49% HF for 20 sec to remove the silicon dioxide layer under the microcantilever.

In order to fabricate the microcantilever with alumina shell structure, 75 nm of alumina is coated on a cantilever with a 3-D nickel inverse opal microstructure in a Cambridge NanoTech atomic layer deposition (ALD) tool. The three edges of the cantilever are cut off in a FIB (FEI DB235). Finally, the microcantilever is soaked in nickel etchant (Transene, type TFB) until the nickel inverse opal structure was fully dissolved. For a wider cantilever, this process takes a longer time.

To measure the spring constant, microcantilevers with a 3-D nickel inverse opal microstructure were fixed on an aluminum block using crystal bond. The measurement was done in an Agilent nanoindenter (MT200) with a Berkovich tip. Because of their softness, the spring constant of microcantilevers with alumina shell microstructure were measured in an Asylum MFP 3D AFM. Resonant frequency and quality factor of both microcantilevers were measured in the AFM.

2.7 Tables

Material	Volume Fraction	Length (μm)	Width (μm)	Thickness (μm)	Spring Constant (N/m)	Resonant Frequency (kHz)	Quality Factor	Effective Young's Modulus (Gpa)
Si	1	342.6	191.9	9.9	107.9	105.7	830	151.0
Si	1	313.5	191.8	9.8	218.9	124.3	461	148.1
Ni	1	330.1	202.5	9.8	247.2	67.7	442	184.3
Ni	1	385.9	128.3	9.5	86.3	47.8	595	180.3
Ni	0.25	399.7	221.9	10.8	47.9	40.1	412	43.4
Ni	0.25	310.4	136.1	9.66	46.0	54.7	658	44.8
Ni	0.22	363.1	224.6	10.9	38.4	39.9	365	25.3
Ni	0.22	459.7	218.3	11.9	26.3	27.7	427	27.6
Ni	0.22	485.7	216.8	12.0	24.9	25.4	646	30.5
Ni	0.22	368.3	145.3	12.4	34.8	42.3	377	25.3
Ni	0.22	375.0	146.0	13.7	40.4	45.6	442	22.6
Ni	0.22	296.0	142.0	10.6	40.0	54.3	549	24.3
Ni	0.15	387.9	215.6	13.0	39.1	52.8	383	19.1
Ni	0.15	418.7	141.4	12.6	19.6	32.7	426	20.2
Ni	0.15	436.6	138.5	10.5	4.9	27.7	427	10.1
Ni	0.15	465.9	142.1	11.1	8.2	22.1	385	17.3
Ni	0.15	292.2	216.0	13.1	52.5	52.6	422	10.8
Al ₂ O ₃	0.08	319.5	92.3	5.2	0.20	17.7	46	2.0
Al ₂ O ₃	0.08	316.0	93.3	4.8	0.22	17.8	43	2.7
Al ₂ O ₃	0.08	327.9	97.8	4.6	0.22	17.0	60	3.8
Al ₂ O ₃	0.08	307.1	105.2	13.58	2.94	50.5	127	1.3

Table 2.1. Comparison of the mechanical properties of microcantilevers with materials and different volume fractions.

2.8 Figures

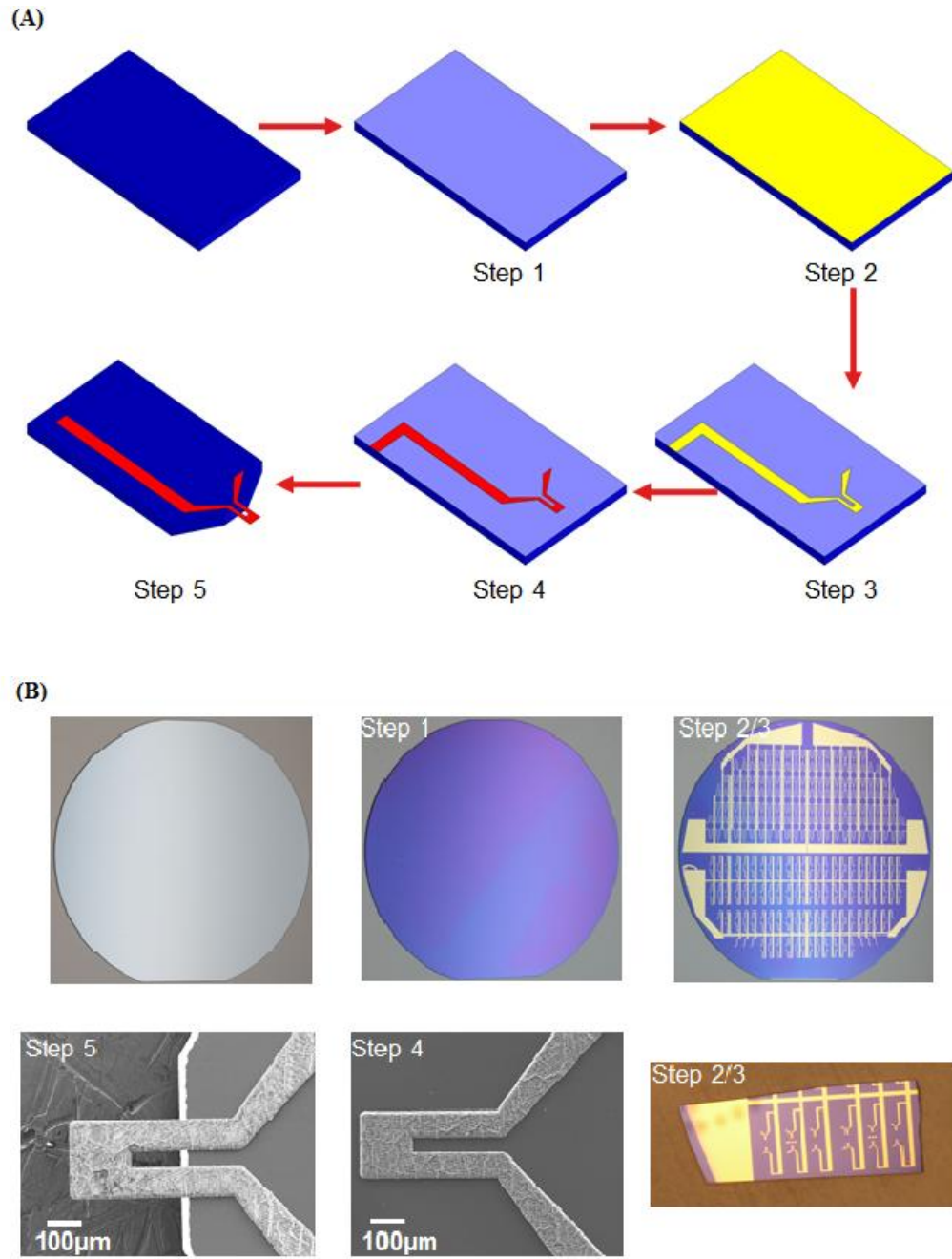


Figure 2.1. (a) The fabrication scheme of the free standing 3-D photonic crystal cantilevers (b) images of the corresponding fabrication step.

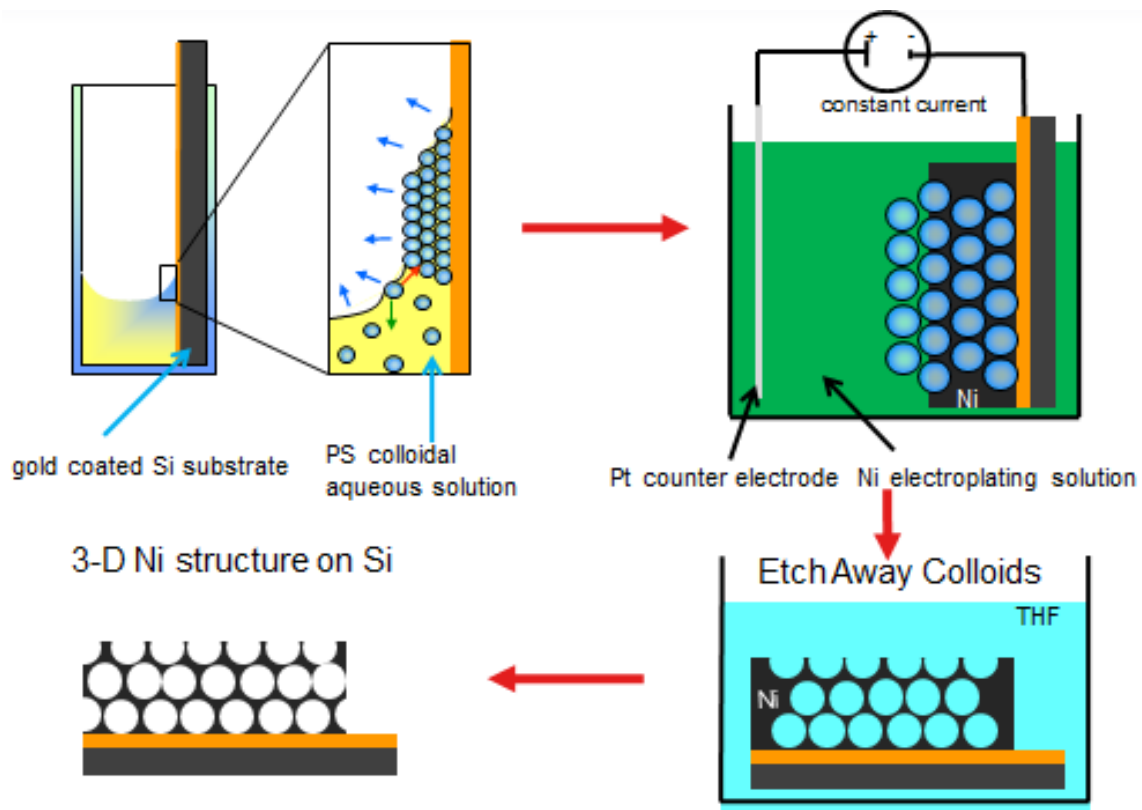


Figure 2.2. The fabrication process of the 3-D photonic crystal cantilevers.

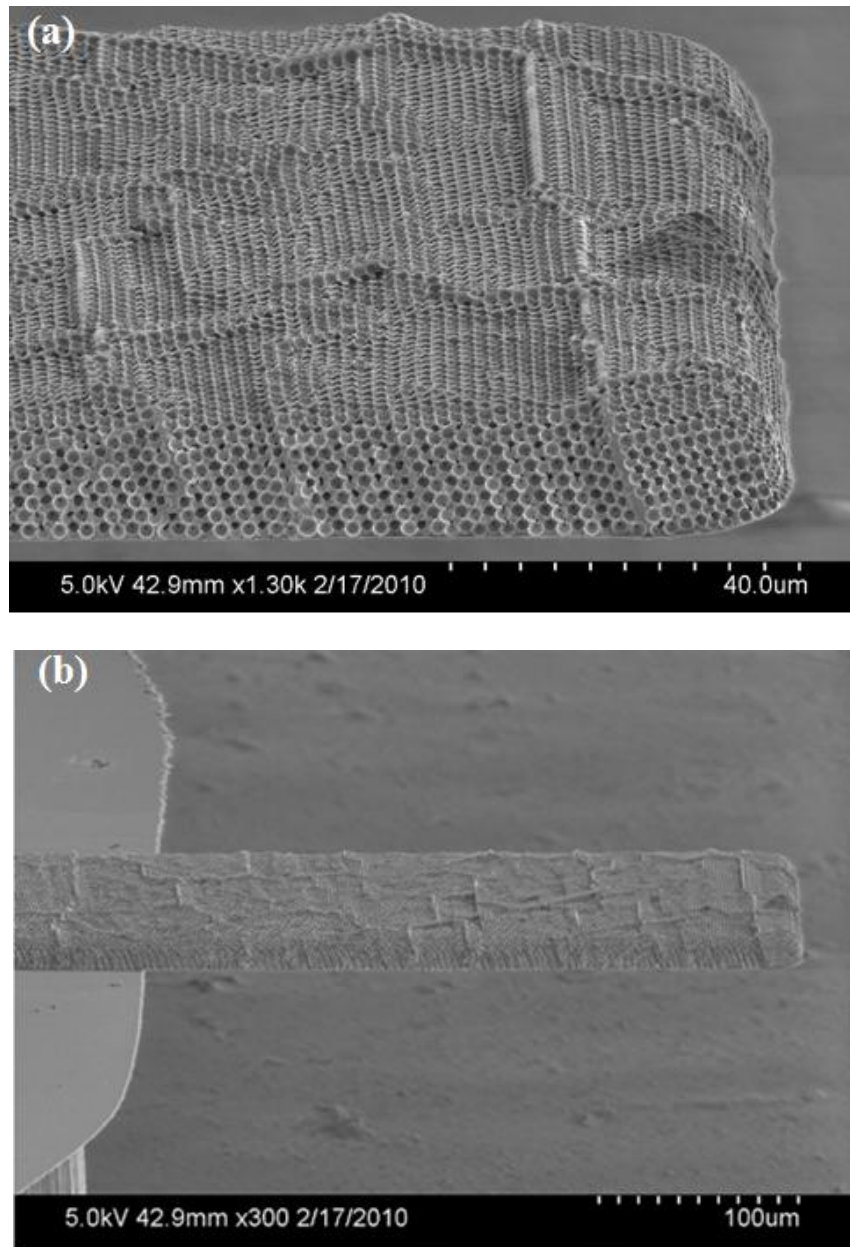


Figure 2.3. SEM images of the cantilever with a 3-D nickel inverse structure. The images show that there are 7~8 layers grown on the substrate.

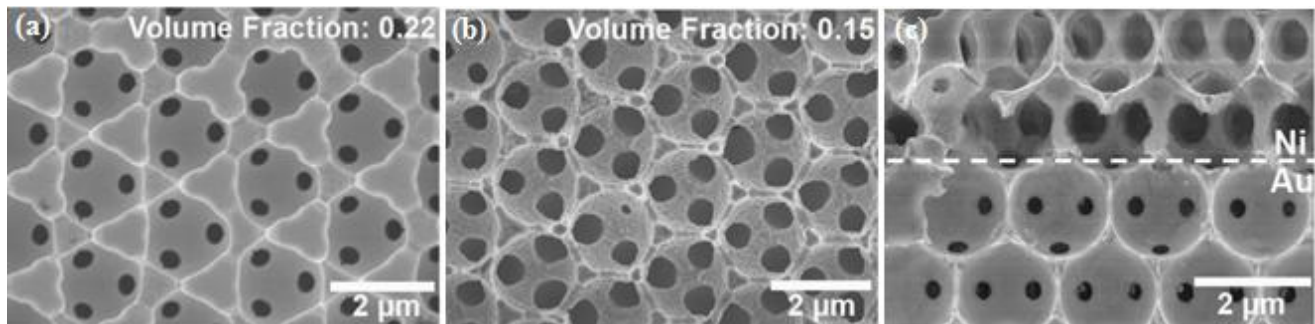


Figure 2.4. a-b) The SEM images of the top view of the cantilever with metal volume fraction of 0.22 and 0.15. c) The SEM image of the cantilever with two different inverse opal microstructures. The bottom metal layer is gold and the top layer is nickel.

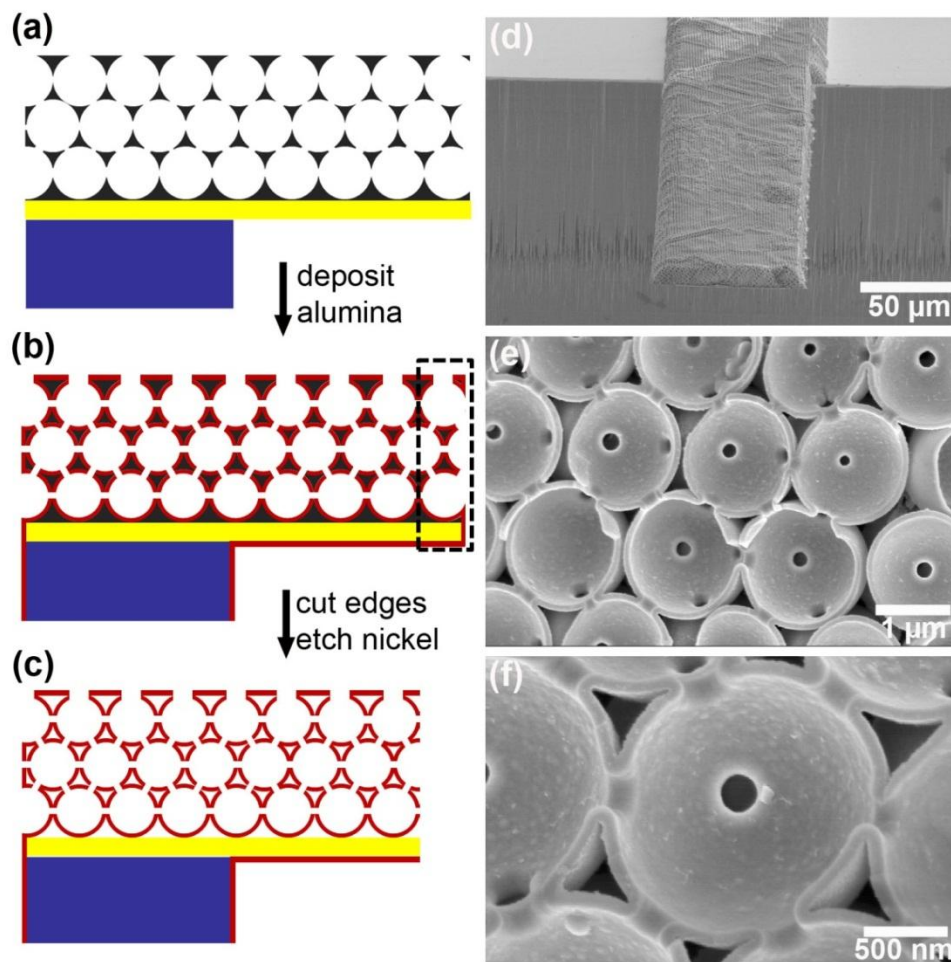


Figure 2.5. a-c) The fabrication scheme of the cantilever containing an alumina shell microstructure. d-f) SEM images of the cantilever containing an alumina shell microstructure.

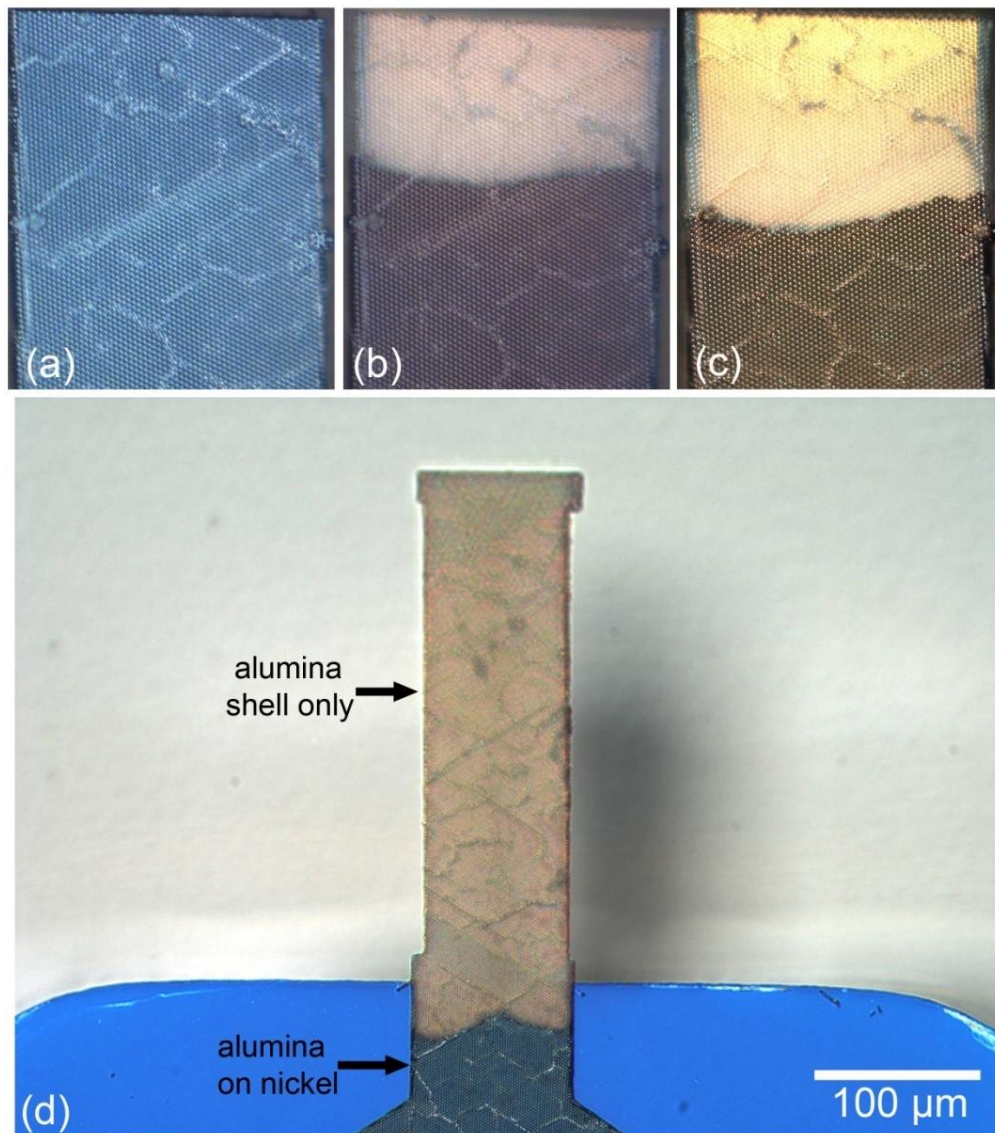


Figure 2.6. a) The optical image of the cantilever containing nickel inverse opal microstructure coated with 75 nm alumina. b-c) The optical images of the cantilever containing nickel inverse opal microstructure coated with 75 nm alumina after dipping into the nickel etchant for 18 hrs. and 24 hrs. d) The optical image of the cantilever containing nickel inverse opal microstructure coated with 75 nm alumina after dipping into the nickel etchant for 7 hrs. Here the nickel in the free standing cantilever is completely removed by the nickel etchant.

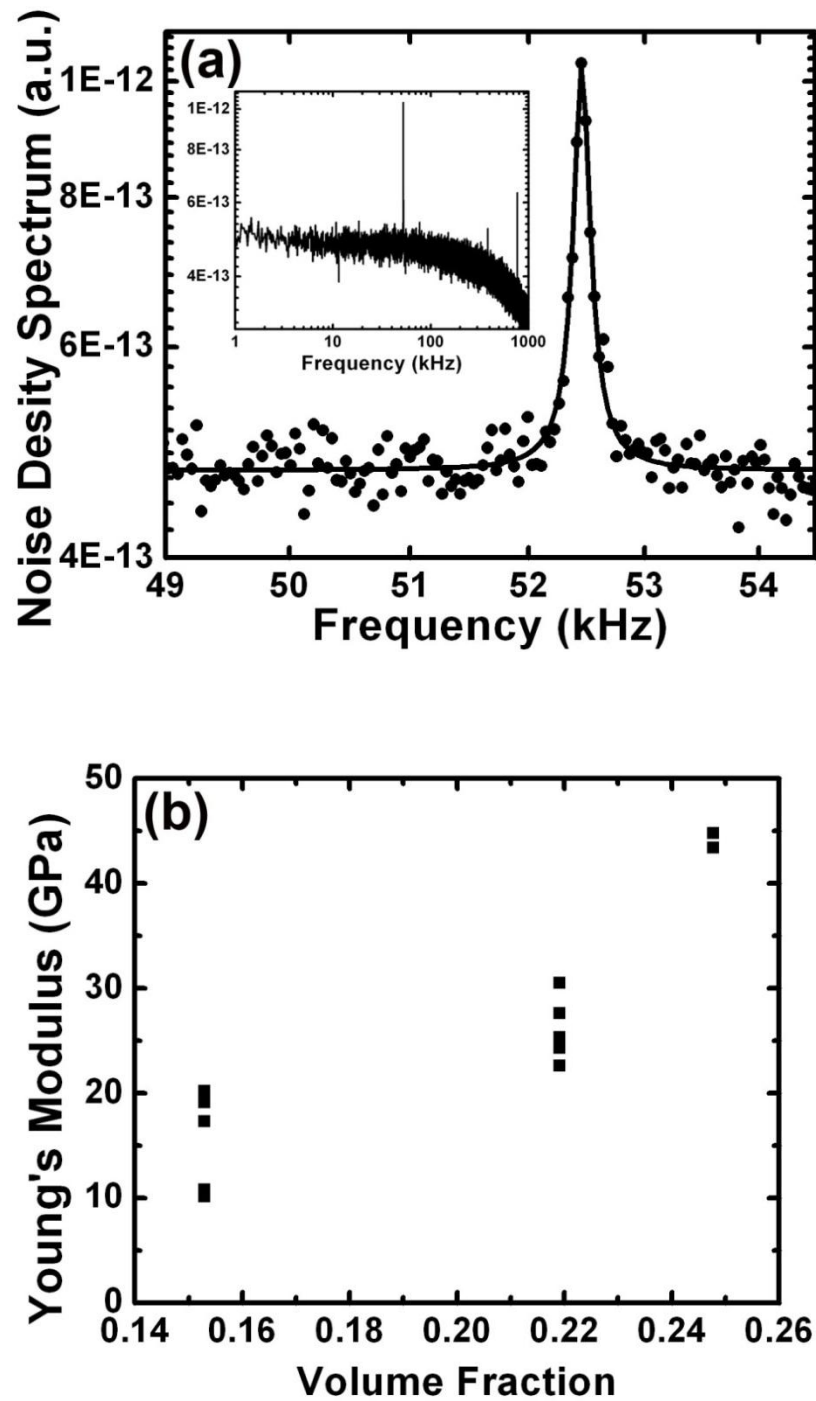


Figure 2.7. The mechanical property measurements of microcantilevers with a 3-D nickel inverse opal microstructure. a) The thermal spectrum measured in an AFM. The inset shows a magnified fundamental resonant frequency. b) The Young's modulus of 3D nickel inverse opal microstructures with different volume fraction.

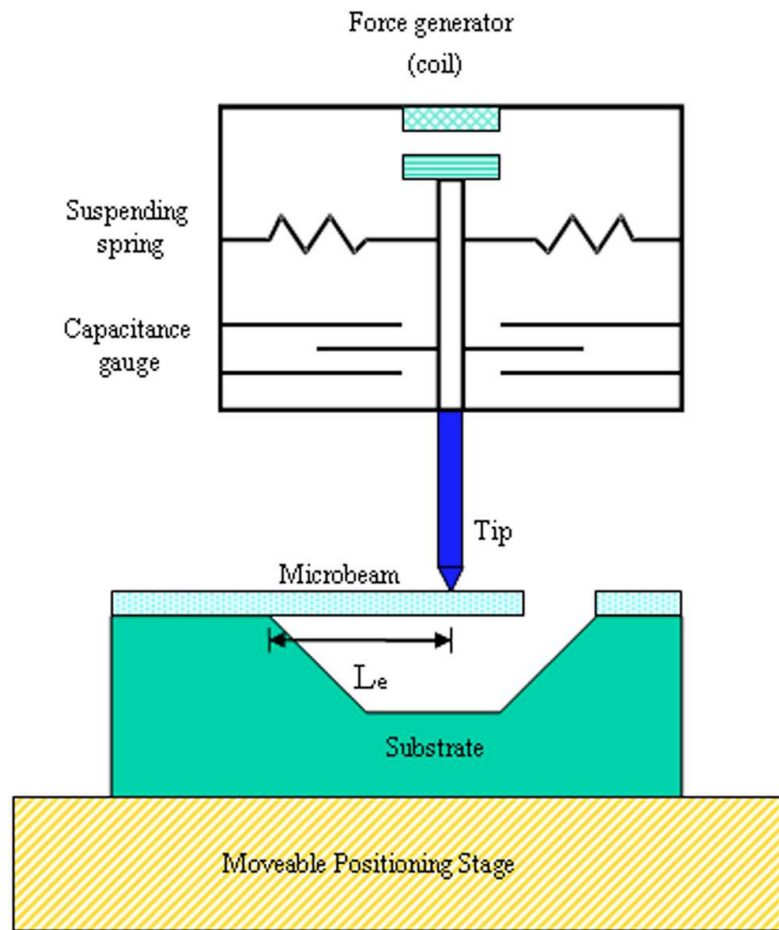


Figure 2.8. The basic scheme of the nanoindenter used to measure the spring constant.

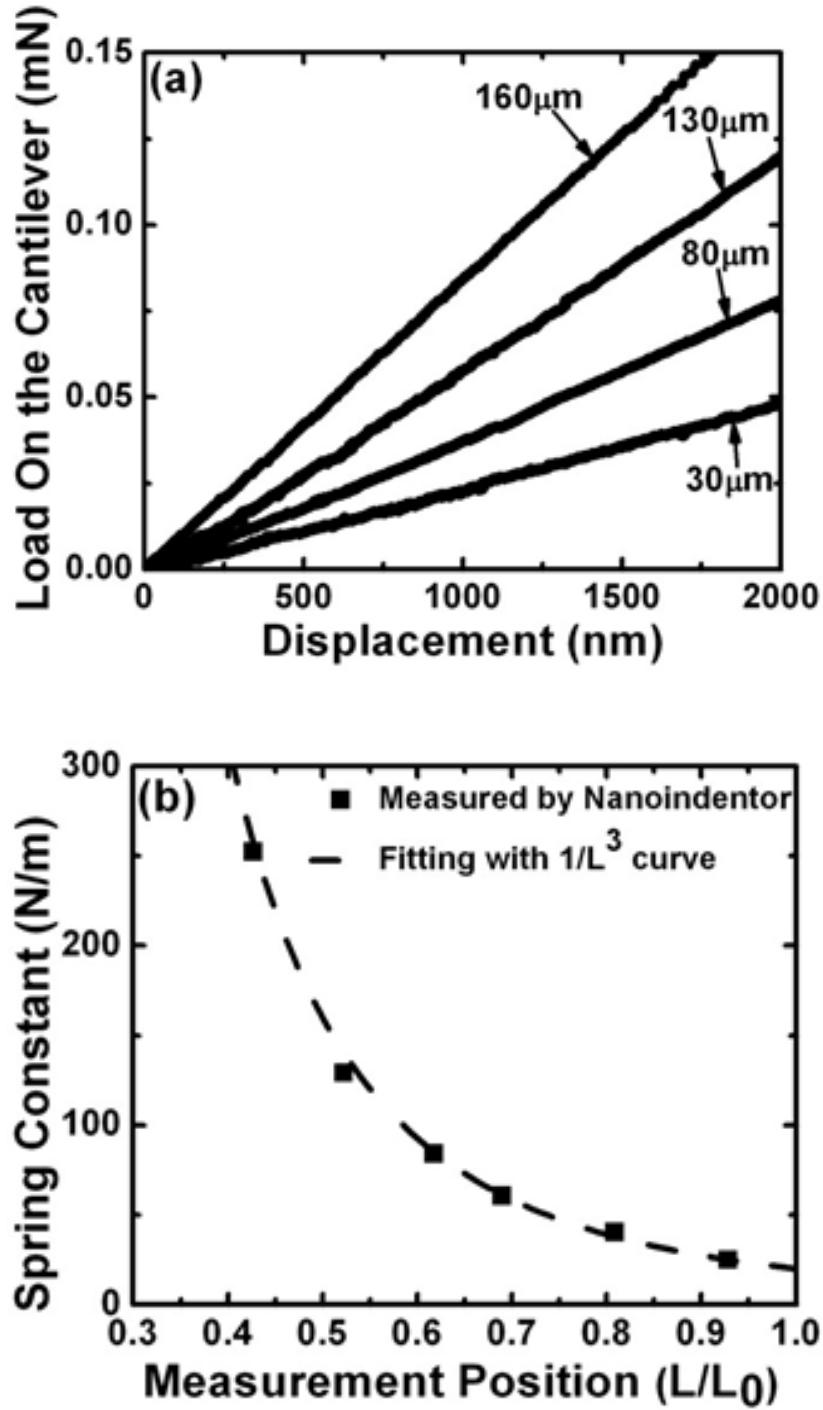


Figure 2.9. The spring constant measurements of the cantilever with 3-D nickel inverse opal microstructure. a) Load-displacement plot of a cantilever with the nanoindenter tip pressed at different distances away from the end of the cantilever. The slope of this curve is the spring constant of the cantilever. b) Fitting of the spring constant measurements with a theoretical model, where L_0 is the length of the cantilever. When L/L_0 equals 1, the value of the dash curve is the spring constant of the cantilever.

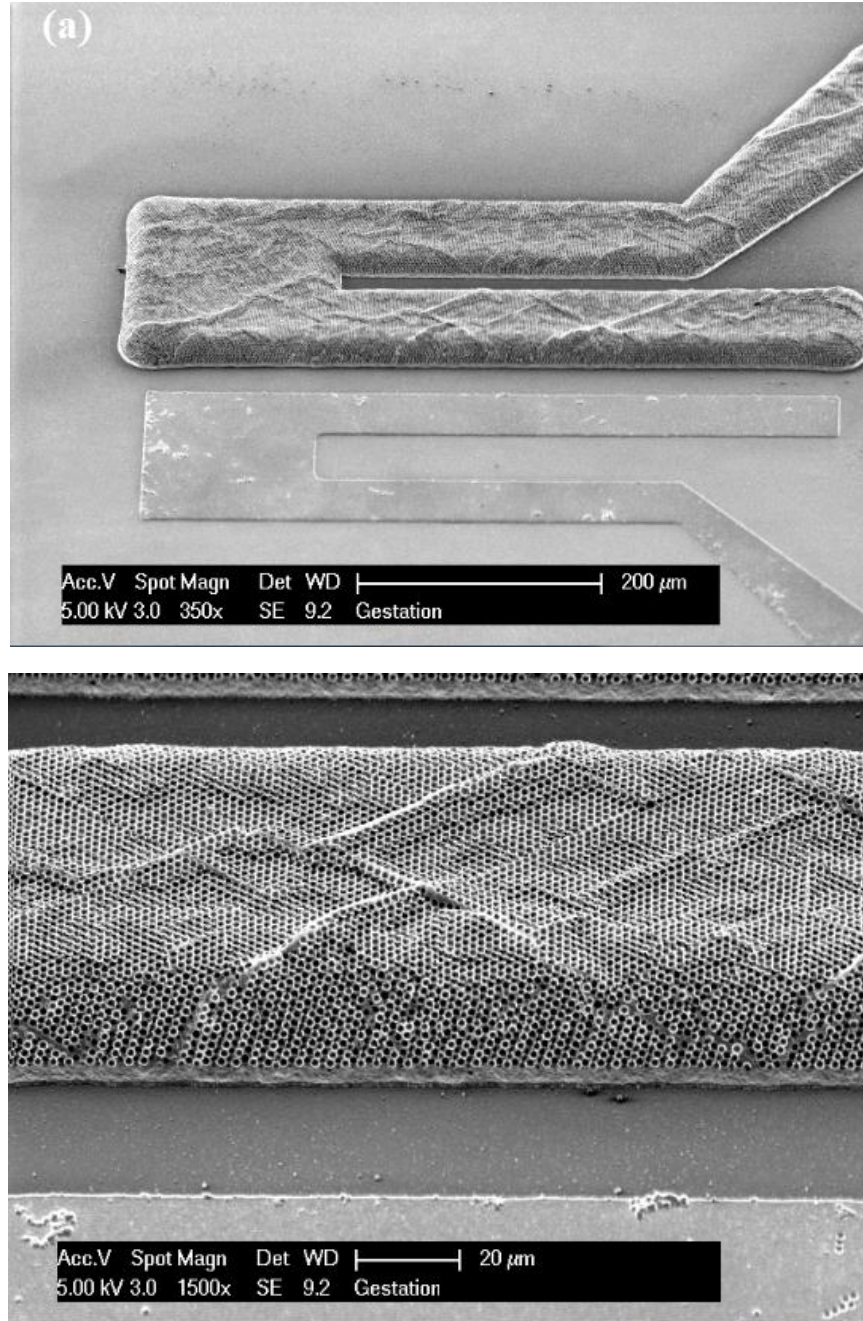


Figure 2.10. The SEM images of the cantilever with a 3-D copper inverse structure. The images show that there are 7~8 layers grown on the substrate.

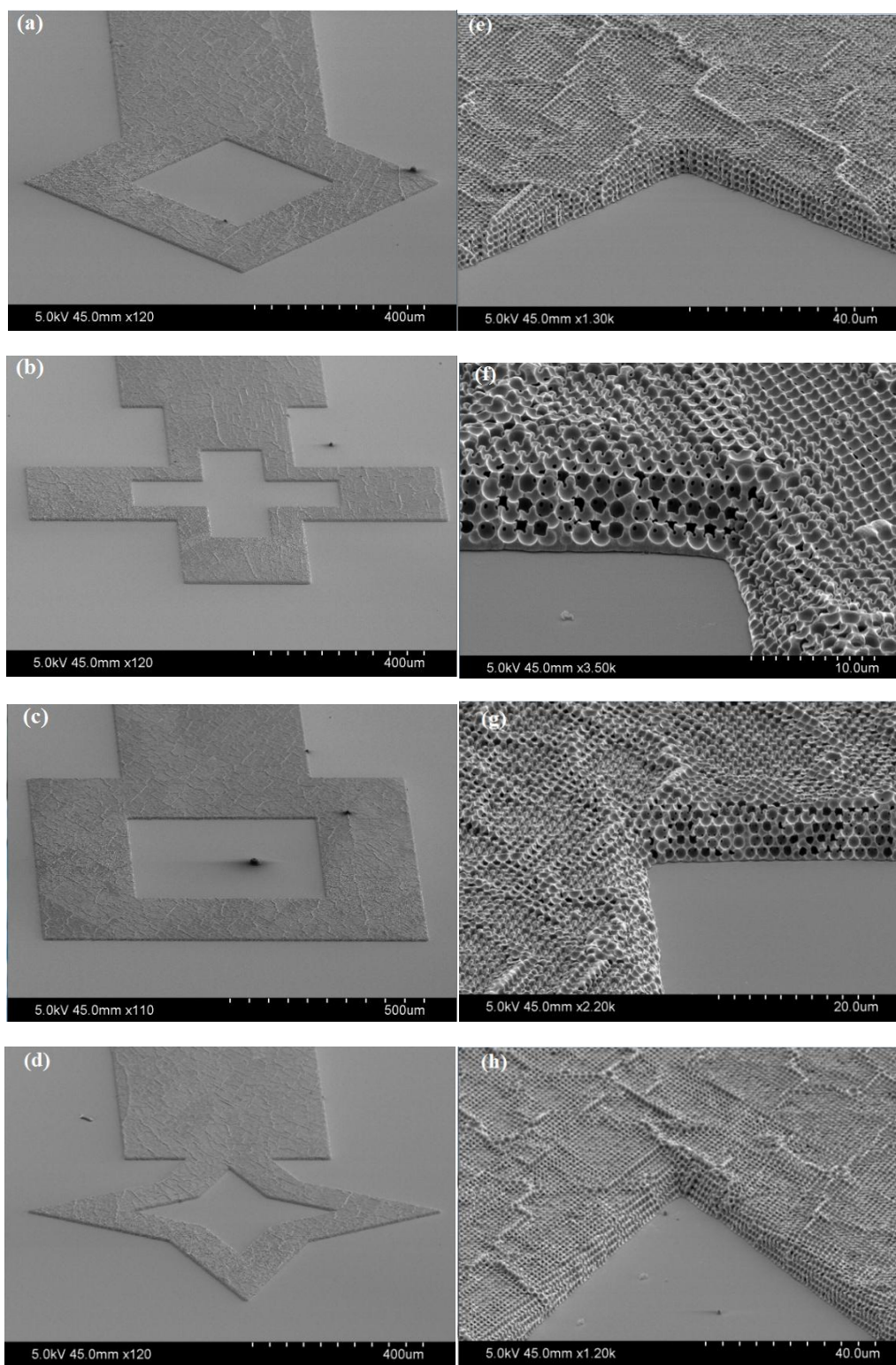


Figure 2.11. The SEM images of the mixed pattern cantilever with a 3-D nickel inverse structure. The images show that there are 5~6 layers grown on the substrate.

2.9 Reference

1. Johnson, S. G.; Joannopoulos, J. D. *Appl. Phys. Lett.* **2000**, 77, 3490.
2. Lin, S. Y.; Fleming, J. G.; Hetherington, D. L.; Smith, B. K.; Biswas, R.; Ho, K. M.; Sigalas, M. M.; Zubrzycki, W.; Kurtz, S. R.; Bur, J. *Nature* **2001**, 414, 289.
3. Vlasov, Y. A.; Bo, X. Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, 414, 289.
4. Yu, X. D.; Lee, Y. J.; Furstenberg, R.; White, J. O.; Braun, P. V. *Adv. Mater.* **2007**, 19, 1689.
5. Jang, J. H.; Ullal, C. K.; Gorishnyy, T.; Tsukruk, V. V.; Thomas, E. L. *Nano Lett.* **2006**, 6, 740.
6. Yang, S. X.; Page, J. H.; Liu, Z. Y.; Cowan, M. L.; Chan, C. T.; Sheng, P. *Phys. Rev. Lett.* **2004**, 93, 4.
7. Tang, J. Y.; Wang, H. T.; Lee, D. H.; Fardy, M.; Huo, Z. Y.; Russell, T. P.; Yang, P. D. *Nano Lett.* **2010**, 10, 4279.
8. Grrin, M.; Trifonov, T.; Rodriguez, A.; Alcubilla, R. *Appl. Phys. Lett.* **2007**, 91, 3.
9. Lee, J. H.; Wang, L. F.; Kooi, S.; Boyce, M. C.; Thomas, E. L. *Nano Lett.* **2010**, 10, 2592.
10. Sypeck, D. J.; Wadley, H. N. G. *Adv. Eng. Mater.* **2002**, 4, 759.
11. Wadley, H. N. G.; Fleck, N. A.; Evans, A. G. *Compos. Sci. Technol.* **2003**, 63, 2331.
12. Chew, X. Y.; Zhou, G. Y.; Chau, F. S.; Deng, J.; Tang, X. S.; Loke, Y. C. *Opt. Lett.* **2010**, 35, 2517.
13. De Angelis, F.; Das, G.; Candeloro, P.; Patrini, M.; Galli, M.; Bek, A.; Lazzarino, M.; Maksymov, I.; Liberale, C.; Andreani, L. C.; Di Fabrizio, E. *Nat. Nanotechnol.* **2010**, 5, 67.

14. Lee, P. S.; Lee, J.; Shin, N.; Lee, K. H.; Lee, D.; Jeon, S.; Choi, D.; Hwang, W.; Park, H.
Adv. Mater. **2008**, 20, 1732.
15. Li, M.; Pernice, W. H. P.; Tang, H. X. *Nat. Nanotechnol.* **2009**, 4, 377.
16. Ozbay, E. *Science* **2006**, 311, (5758), 189-193.
17. Cole, R. M.; Sugawara, Y.; Baumberg, J. J.; Mahajan, S.; Abdelsalam, M.; Bartlett, P. N.
Physical Review Letters **2006**, 97, (13).
18. Ebbesen, T. W.; Lezec, H. J.; Ghaemi, H. F.; Thio, T.; Wolff, P. A. *Nature* **1998**, 391, a.
(6668), 667-669.
19. Viani, M. B.; Schaffer, T. E.; Paloczi, G. T.; Pietrasanta, L. I.; Smith, B. L.; Thompson, J.
B.; Richter, M.; Rief, M.; Gaub, H. E.; Plaxco, K. W.; Cleland, A. N.; Hansma, P. K. *Rev.*
Sci. Instrum. **1999**, 70, 4300.
20. Lee, P. S.; Mangelinck, D.; Pey, K. L.; Ding, J.; Dai, J. Y.; Ho, C. S.; See, A.
Microelectronic Engineering **2000**, 51-2, 583-594.

CHAPTER 3

Dye Sensitized Solar Cells Using 3-D Transparent Conductive Oxide

3.1 Introduction

There are many solar cell types being proposed world-wide as solutions for energy problems. The technology proposed here, along with other technologies has the potential to develop sustainable power generation. Although dye sensitized photovoltaic cell have been used in the past due to its enhancement in the optical density, because of its increase in the charge transport path length it has not been the best system. An effective approach to solve this problem is to enhance the interface area between the transparent conducting oxide (TCO) and the semiconductor layer. In this paper, 3-D inverse opal fluorinated tin oxide (IO-FTO) electrode is introduced. The photonic crystal structure containing an IO-FTO shows a strong light trapping capability. Also we introduce a mesoporous TiO_2 structure inside the tin oxide inverse opal structure. These mesoporous films contain physisorbed and trapped dye, which dominates the emission.

3.2 Solar Cells

3.2.1 Photovoltaics

Conventional silicon solar cell is a well-known solar cell which is also called as photovoltaic cells. Two types of doping are used in the conventional silicon cell. One is n-doping, which results in a free electron and the other is p-doping, which is the lack of electron. When these two crystals are combined together, the free electron tends to move from n-doped crystal to the p-doped crystal to fill the electron hole. As the solar radiation hits the surface of the cell, the photons in the light excites the valence electrons of p-doped crystals and this photoexcited free

electrons move to the n-doped crystal. The electron is then transferred from the n-doped crystal to the p-doped crystal to fill the electron hole. Thus, the current is produced by using the solar radiation. In practice, this is formed by defining within the crystalline silicon cell two kinds of silicon layers. The first one is the layer where the sun light hits. This region is negatively doped with phosphorus. The other layer is the layer positively doped with boron. At the boundary layer, the charge separation tends to occur. Metallic contacts allow the power to move outside of the cell.

However, there are problems in photovoltaic cells. For example, some of the ejected electrons from the p-doped area are taken from the other p-doped crystals in the system. This is one of the major factors that lower the efficiency of the conventional photovoltaic solar cells. Since some photons have a higher energy than the required energy for photo excitement, the remaining energy is transformed into heat after the photo excitement. Also, silicon is an expensive material and many practical obstacles exist to reduce the cost of processing silicone [1]. Because of these problems, different types of solar cell systems have been developed and introduced.

3.2.2 Dye Sensitized Solar Cell (DSSC)

The dye sensitized solar cells (DSSCs) are based upon the sensitization of mesoporous, nanocrystalline metal oxide films to visible light by the adsorption of molecular dyes. Photoinduced electron injection from the sensitizer dye into the metal oxide conduction band initiates charge separation. Subsequently, the injected electrons are transported through the metal oxide film to one device electrode, while a redox-active electrolyte is employed to reduce the dye cation and transport the resulting positive charge to a platinum counter electrode [2].

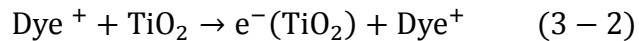
The first dye sensitized solar cell (DSSC) was introduced by Grätzel in 1991, with an energy conversion efficiency of 7.1% [3]. This is a system which mimics the photosynthesis in terms of transforming the solar energy to another form of energy which is electricity. It was also reported that 11 % efficiency is attained for a DSSC [4]. A typical DSSC achieved more than 10% sunlight to electrical power conversion efficiency [5] while 15-17% conversion efficiency has been attained by typical commercial silicon solar cell modules [6]. A typical DSSC is composed of a wide band gap oxide semiconductor, an electrolyte, a sensitizer (dye) and a counter electrode as it is shown in Figure 3.1. On the anode side of the cell, dye is adsorbed on the semiconductor oxide which is sintered on Transparent Conducting Oxide (TCO) glass. On the cathode side, there is another TCO with a catalyst coating over it. A redox electrolyte fills the gap between two TCO glasses. In general, semiconductor of choice is titanium dioxide, electrolyte couple is iodide/triiodide, counter electrode is platinum and the dye is normally ruthenium base [7]. The principle of the DSSC process was mentioned above but the following explains in more detail; the sensitizer is photoexcited by adsorbing the incident solar rays. After the sensitizer is excited, it then injects its electron to the conduction band of the oxides which is anchored to the sensitizer. Then, the excited sensitizer is regenerated by the electron from electrolyte which is a redox couple. After the oxidized dye is regenerated by taking electron from the iodide and forming triiodide, the iodide is regenerated by the triiodide at the counter-electrode. Cycle is completed by electron migration between TiO_2 (anatase) and the counter-electrode which is usually platinum coated TCO. The electron cycle in the cell was studied by Grätzel in 2001 [8] and is given in Figure 3.2 [5, 9]. However, a monolayer of dye can absorb very limited amount of solar energy due to the limited cross section area of the dye molecules. Also, multilayer application of dye is not a solution because the layers filter the solar arrays. This

problem can be resolved by using mesoporous nanosize TiO_2 . The mesoporous nanosized TiO_2 is used to increase the total surface area. It is emphasized that, solar arrays are absorbed by the dye covered nanooxide sponge better due to the increase of the surface area. Surface gets significantly larger for a 10 μm mesoporous nano-thick oxide film which means that the efficiency in sunlight captured by dye covered oxide gets much larger [8]. There are alternative wide band gap oxides such as ZnO and Nb_2O_5 that can also be used as semi-conductor oxide. However TiO_2 is most preferred because it is abundant. There are two main regeneration phase systems in a DSSC which is the solid state DSSC and the liquid state DSSC. DSSC using a liquid electrolyte includes a redox couple to regenerate the sensitizer. The electrolyte is composed of an organic solvent and I/I^3 redox couple. The main purpose of the electrolyte is to improve the regeneration of DSSC. The I^- ion in the electrolyte regenerates photo excited dye molecule. Voltage produced by DSSC is the difference between the chemical potential of the titanium dioxide (Fermi level) and the redox potential of the electrolyte. The main reactions proceeding in the system are described by Smestad [10], Hauch and George [7]. The reactions are the following;

Dye molecule is photo excited



The electrons are then ejected to the conduction band of the semiconductor oxide



The dye molecule is reduced by the electrolyte couple with the reaction



Iodide is regenerated by taking the electron at the cathode (Pt)



The cathode is used to regenerate the electrolyte couple which in turn, regenerates the photo excited dye molecule. In other words, counter electrode is responsible for catalytic cathodic reduction of triiodide to iodide. Although many other materials like carbon and conductive polymer are used, platinum is still the most preferred material due to its high catalytic activity for triiodide / iodide reduction and its light reflectivity is at an acceptable amount.

Many platinum coating techniques are used like electron beam evaporation, sputtering, thermal decomposition, electrodeposition and thermal treatment for platinization of the cathode. The efficiency of a DSSC strictly depends on the sensitizer of choice. Following properties for a sensitizer are quite important. Absorption spectrum of the dye is critical because the dye needs to adsorb the visible light. Also, the redox properties of the ground state and the excited state of the dye molecule have to be examined. This is because both electron transfer between the sensitizer and the electrolyte, and between the sensitizer and TiO_2 strictly depends on this criteria. Energy levels of the dye and the semiconductor oxide must be proper such that electrons can be transferred from dye molecule to the semiconductor oxide as it is described in Figure 3.2. Also, the dye should be regenerated fast enough after the electron is loose. Finally, the dye should be stable for about years of exposure to natural light for being economically feasible [8]. It is reported that Ru and Os based sensitizers are the best molecules. Recent reports indicate that better sensitizer known as the black dye adsorbs in the near-IR is better than N3 [8, 11, 12].

3.3 3-D Transparent Conductive Oxide DSSC

3.3.1 The Preparation of Silica Opal Template

Transparent Conducting Oxide having the dimensions of 5 cm × 5 cm and a thickness of 2.2 mm was used as a conducting glass. This has a fluorine doped tin oxide ($\text{SnO}_2\text{:F}$) layer on the one side which is also known as FTO glass (Tec 15, Hartford Glass Co. Inc. $8\Omega/\text{sq}$). Then we prepare the silica solution. In this experiment we use both 4 μm and 10 μm size silica particles. The silica particle stock solution is prepared by adding methanol and ethanol in a 1:1 ratio to the silica particles (4 g) so that the total volume is 10 mL (20 volume percent). This mixture is sonicated until all the silica particles fully dispersed. While the sonication is running some of the ethanol tend to evaporate even though it is sealed. If some particles are still left in the solution undispersed this can be separated from the solution. Then we add 1 mL of DMF and 2 mL of 2-methoxyethanol to complete the stock solution. This stock solution is sonicated again.

However if we only use the silica particles to prepare the template, the neck size between the particles is too small. This will be a problem when etching the silica particles. Because of this reason selective deposition of inorganic materials at the neck area is required. The materials should be thermally stable at 500 °C and needs to be easily removed. We selected methacryloxypropyltrimethoxysilane (MSQ) to mix with the stock solution. 2 g of the stock solution is mixed with 0.5 g of 10 wt. % MSQ in order to make a silica 2 wt. % MSQ solution.

We now spin coat this 2wt. % MSQ solution onto a clean FTO glass at 800 rpm for 1 minute shown in Figure 3.3. Before rotating the spin coater we wait for 15 seconds in order for the particles to settle down. After the particles are spun for 1 minute, finally we finish by heating

the samples at 450 °C for 1 hour with a heating rate of 5 °C/ min. The thickness has been differed by going through the spin coating process once and twice.

3.3.2 Tin Oxide Inverse Opal

The inverse opal structure here is different from the one mentioned in Chapter 2. In this experiment we use chemical vapor deposition (CVD) in order to deposit Tin Oxide (SnO_2). Of course there are many other methods to deposit SnO_2 such as dipping method and spin coating. There are two different gas lines connected to this system; one is air-line and the other is nitrogen line. The nitrogen line goes through the precursors and the air-line meets with the nitrogen line right before it goes into the system. As the nitrogen gas goes through the two precursors; tin tetrachloride (Acros) and trifluoroacetic acid (TFA) (Sigma-Aldrich), it forms a conformal SnO_2 coating on the silica opal substrate. The CVD process is done for 3.5 hours. After SnO_2 is conformally deposited on the silica opal template, RIE is done in order to etch the top surface of the SnO_2 . The SEM image of the silica particles with SnO_2 deposited on the surface after performing RIE is shown in Figure 3.5. Then we remove the silica particles by dipping it in water diluted 5 wt. % HF for 2~3 hours. However if the SnO_2 is not deposited well enough, the structure tends to delaminate when etching the silica particles. We use a same process in order to make TiO_2 inverse opal structure. We use titanium tetrachloride (TiCl_4) (Acros) and ethyl acetate (Sigma-Aldrich) instead. However, we do not use this structure due to the delamination problem mentioned above.

3.3.3 Mesoporous Titania

To form a mesoporous titania layer inside the SnO_2 inverse opal structure, we use TiO_2 solution. In order to make the TiO_2 solution, we mix 78 mL of water and 22 mL of TiCl_4 (Acros)

and put it in ice bath for 1 hour. After the stock solution is made, we immerse the SnO₂ inverse structure upside down in a vial containing the TiO₂ solution. Then the vial is kept in the oven (70 °C). The vial is cooled to room temperature and the final SnO₂ inverse opal with titania mesoporous structure is made shown in Figure 3.6. Finally the sample is rinse dried and cut into the size shown in Figure 3.8 and sent to Samsung SDI (South Korea) to assemble the finalized DSSC. For the dye, N719 dye is used. The Structure and Absorbance of the dye, N719 is shown in Figure 3.10.

3.4 Characterization of DSSC

The voltage-current measurements of several different samples were done by the multimeter. The schematic illustration of the current-voltage measurement setup is shown in Figure 3.9. The positive electrode of the multimeter was connected to the counter electrode of the DSSC and the negative electrode of the multimeter was connected to the electrode containing SnO₂ inverse opal structure with titania mesoporous structure. It was assumed that the multimeter had an infinite resistivity and the battery of the multimeter is ideal. In order to compare different cells, current-voltage curves of the cells are used. For overall cell efficiency, the most important parameters are open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and the maximum power point (P_{MPP}). Also voltage at the maximum power point (V_{MPP}) and current at the maximum power point (i_{MPP}) can be used. Another important parameter is the filling factor (FF) which is defined as the ratio of maximum power of the cell found from voltage-current curve to the theoretical maximum whose formula is given by equation (3.5-3.9).

$$FF = P_{MPP}/V_{OC} \times I_{SC} \quad (3 - 5)$$

These parameters are important for calculating the efficiency of the solar cell. The following equations are valid:

$$R = V/i \quad (3 - 6)$$

$$P = V \times i \quad (3 - 7)$$

Efficiency of a solar cell (η) is expressed as the ratio of maximum power point to solar irradiance hitting to the panel surface.

$$\eta = P_{MPP}/(E \times A) = (FF \times V_{OC} \times I_{SC})/(E \times A) \quad (3 - 8)$$

where A is the effective area of the cell and E is the solar irradiance.

The current density (j) is another parameter that is used frequently for calculations and defined as given in (3-9)

$$j = i/A \quad (3 - 9)$$

The sample calculation for active area, short circuit current, open circuit voltage, filling factor and efficiency is given in Table 3.1. Also the voltage current plot is shown in Figure 3.11. The current is linearly proportional to the solar irradiance. A straight line is expected between the current and solar irradiation. Voltage increases with solar intensity sharply up to 100 W/m² and still increases slightly after 100 W/m² with the intensity [5].

It is seen in Table 3.1 that when comparing between the 4 μ m samples and 10 μ m samples, even though the filling fraction decreased the current value and the efficiency increased. Also when the thickness of the 10 μ m increased, there was not a significant change but still there was a small decrease in the current value and the efficiency. In addition to this result, we also compared the 10 μ m samples differing the mesoporous titania layer. In theory, as the mesoporous titania layer gets thicker the current value as well as the efficiency. When comparing the 10 μ m SnO₂ inverse opal structure that contains 4 cycles of mesoporous titania spin coating with 10 μ m SnO₂ inverse opal structure that contains 6 cycles of mesoporous titania spin coating, we can see this trend. However, when comparing the 10 μ m SnO₂ inverse opal structure that

contains 6 cycles of mesoporous titania spin coating with 10 μm SnO_2 inverse opal structure that contains 8 cycles of mesoporous titania spin coating, we cannot see this trend. But the difference is not significant. This might occur due to the over layer that forms on the top surface shown in Figure 3.13. If we remove the over layer and sinter the sample, the shrinkage will allow the blockage to open. This opening will allow more mesoporous titania to inside the inverse opal structure. In result, we will not only achieve a higher filling ratio but also a higher efficiency of the DSSC.

3.5 Conclusion

We have been able to fabricate 3-D Transparent Conductive Oxide DSSC using SnO_2 inverse opal structure along with a titania mesoporous structure. The tin oxide has a lower absorption and it act as a better acceptor. Also when comparing between the samples using 4 μm silica particles and the samples using 10 μm silica particles, the samples using 10 μm silica particles will have a higher loading of titania close to the FTO glass. It will have less amount of FTO which will lower the absorption at the FTO structure. The fabrication process of the 3-D SnO_2 inverse structure FTO electrode containing mesoporous titania is shown in Figure 3.7. In order to increase the neck area, we incorporated 2% MSQ to the silica particles when fabricating the silica opal template shown in Figure 3.3. In addition we were able to deposit relatively thick SnO_2 layer using chemical vapor deposition shown as Figure 3.4. After RIE when we infill the SnO_2 inverse opal structure with mesoporous titania layer using spin coating, the first run works well. However, as we perform more and more cycling, it will form an over layer on the top surface. This prevents the TiO_2 solution to go into the inverse structure which affects (lowers) the filling fraction. Figure 3.11 shows the current versus voltage plot and the Table 3.1 shows the active area, short circuit current, open circuit voltage, filling fraction, and efficiency values of the

various samples. Most of the data plots make sense, but there are still more data in order to prove that the inverse opal structure along with the mesoporous structure. Also more data is needed to prove that using larger silica particles will have advantage over using smaller silica particles.

3.6 Experimental

In order to fabricate a 3-D Transparent Conductive Oxide DSSC using SnO_2 inverse opal structure with mesoporous titania structure inside, we start by preparing a silica opal template. First we add methanol and ethanol in a 1:1 ratio to the silica particles (4 g) so that the total volume is 10 mL. This solution was sonicated and mixed with 1 mL of DMF and 2 mL of 2-methoxyethanol to make the silica stock solution. After sonicating the stock solution once more, we mix 2 g of this stock solution with 0.5 g of 10 wt. % MSQ in order to make a silica 2 wt. % MSQ solution. We now spin coat this 2wt% MSQ solution onto a clean FTO glass (Tec 15, Hartford Glass Co. Inc. $8\Omega/\text{sq}$) at 800 rpm for 1 minute. Before rotating the spin coater we wait for 15 seconds in order for the particles to settle down. After the particles are spun for 1 minute once or twice, finally we finish by heating the samples at 450 °C for 1 hour with a heating rate of 5 °C/ min.

The process of developing a SnO_2 inverse opal starts by depositing SnO_2 chemical vapor deposition (CVD). Tin tetrachloride (Acros) and trifluoroaceticacid (TFA) (Sigma-Aldrich) are used as a precursor and the system was running for 3.5 hours. After conformal SnO_2 layer is deposited on the silica particles, RIE was done for 40 minutes. When the top surface of the SnO_2 coating is etched we use 5 wt. % water diluted HF solution to etch away the silica particles.

To form a mesoporous titania layer inside the SnO₂ inverse opal structure, we use TiO₂ solution. In order to make the TiO₂ solution, we mix 78 mL of water and 22 mL of TiCl₄ (Acros) and put it in ice bath for 1 hour. After the TiO₂ solution is made, we immerse the SnO₂ inverse structure upside down in a vial containing the TiO₂ solution. Then the vial is kept in the oven (70 °C). The vial is cooled to room temperature and the final SnO₂ inverse opal with titania mesoporous structure is made. Finally the sample is rinse dried and cut into the size shown in Figure 3.8 and sent to Samsung SDI (South Korea) to assemble the finalized DSSC as mentioned before. For the dye, N719 dye is used [13].

3.7 Tables

	active area	Jsc (mA/cm ²)	Voc (V)	f.f	Effi. (%)
4 μm_1	0.3	8.36	0.77	60	3.8
10 μm_1	0.3	9.34	0.76	56	4.0
10 μm_2	0.3	9.17	0.74	56	3.8
4cy_1	0.3	4.28	0.76	60	2.0
6CY_1	0.3	8.25	0.75	57	3.6
8cy_1	0.3	7.49	0.76	55	3.1

Table 3.1. The active area, short circuit current, open circuit voltage, filling factor and efficiency of various samples; 4 μm_1 is the sample using 4 μm silica particles (spin coat once), 10 μm_1 is the sample using 10 μm silica particles (spin coat once), 10 μm_2 is the sample using 10 μm silica particles (spin coat twice), and the rest are the samples using 10 μm silica particles (spin coat once) and differing the number of mesoporous titania spin coating cycles done on the SnO₂ inverse opal structure.

3.8 Figures

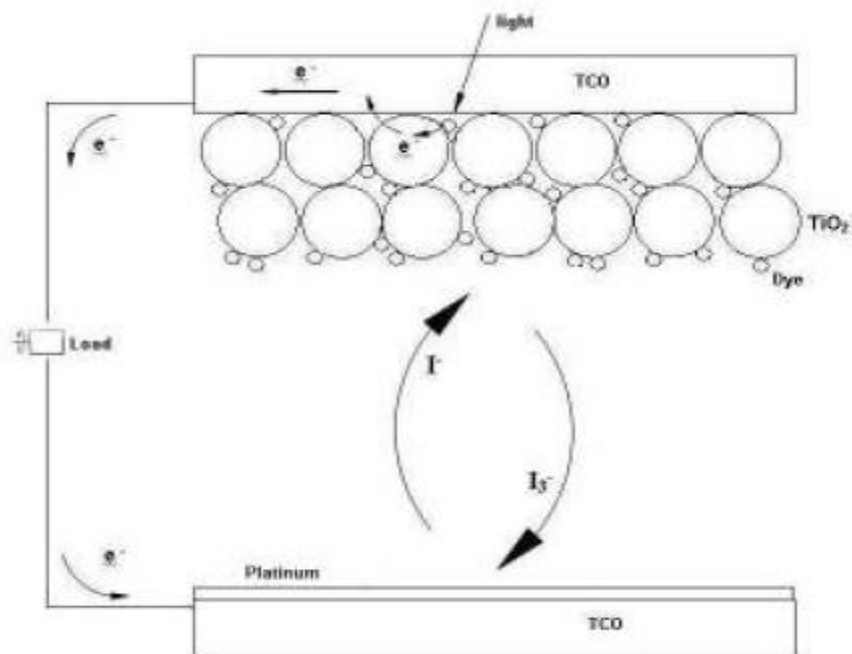


Figure 3.1. The operating principle of the DSSC [5].

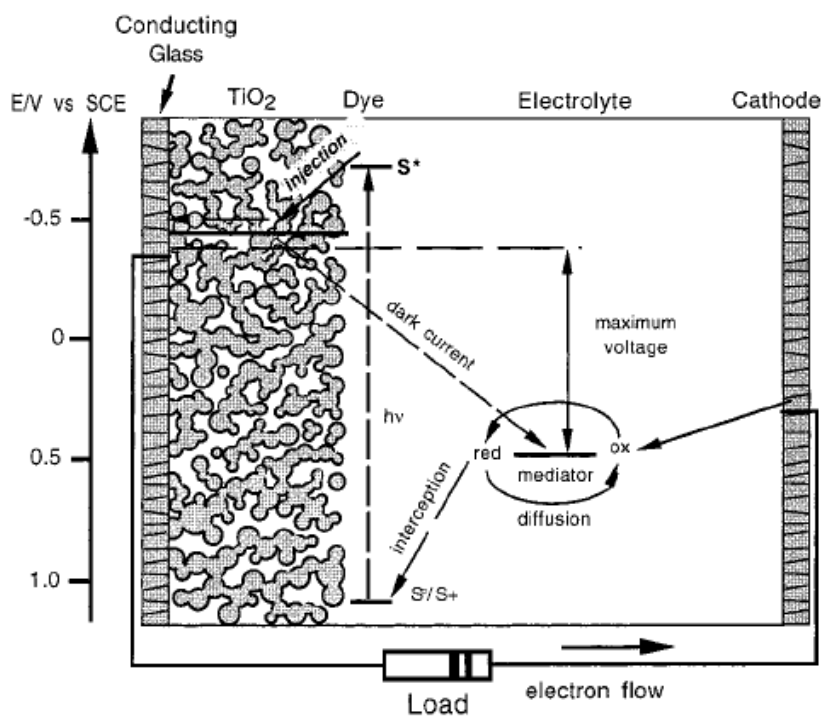


Figure 3.2. Electron cycle in the DSSC [8].

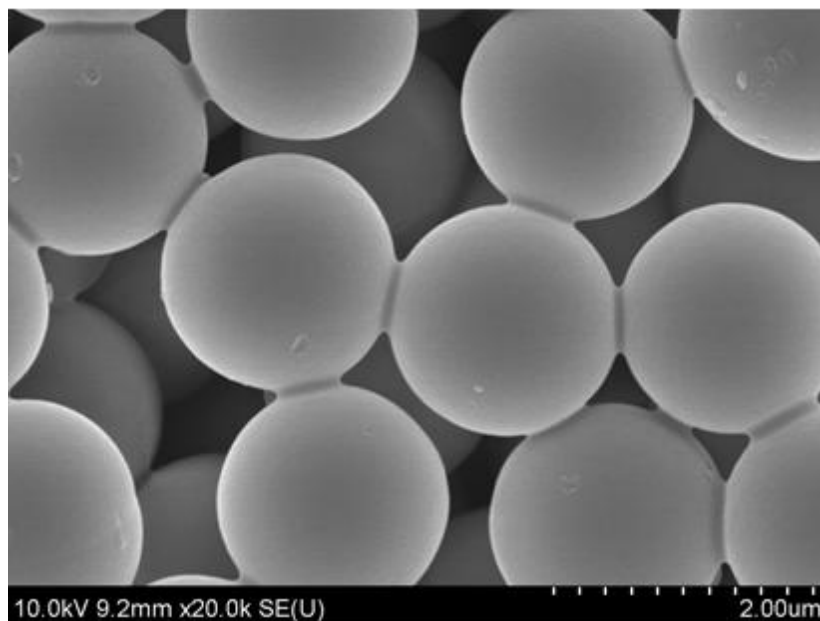


Figure 3.3. The SEM image of the silica particles with MSQ mixed with it. The sample is heat treated at 500 °C for 1 hour.

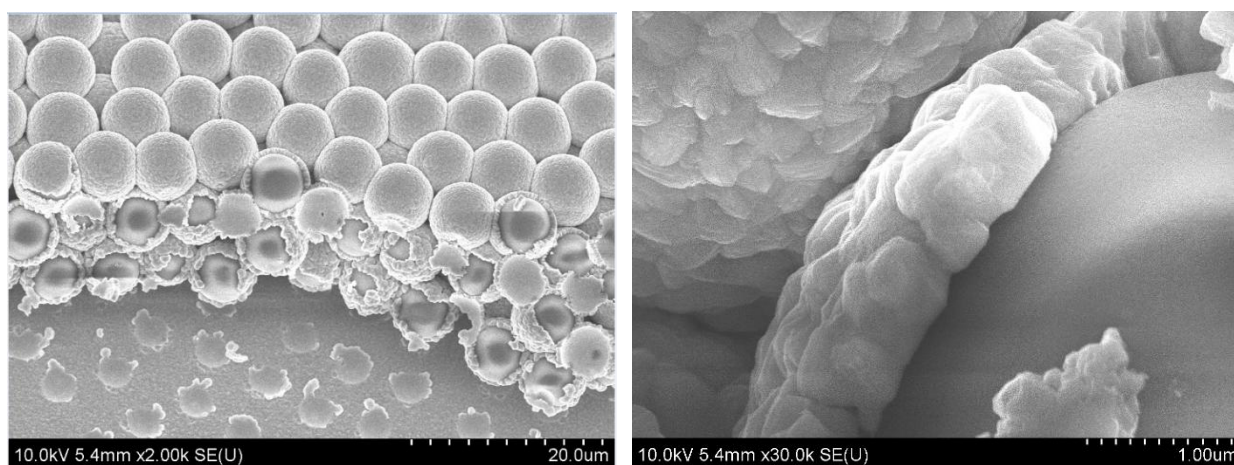


Figure 3.4. The SEM images of the silica particles with SnO₂ deposited on the surface.

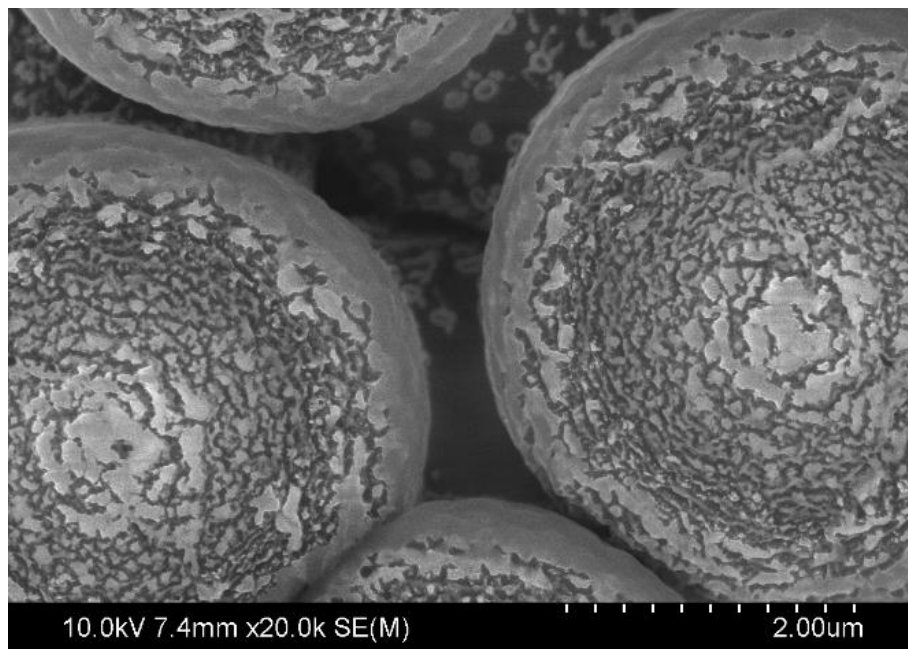


Figure 3.5. The SEM image of the silica particles with SnO₂ deposited on the surface after performing RIE.

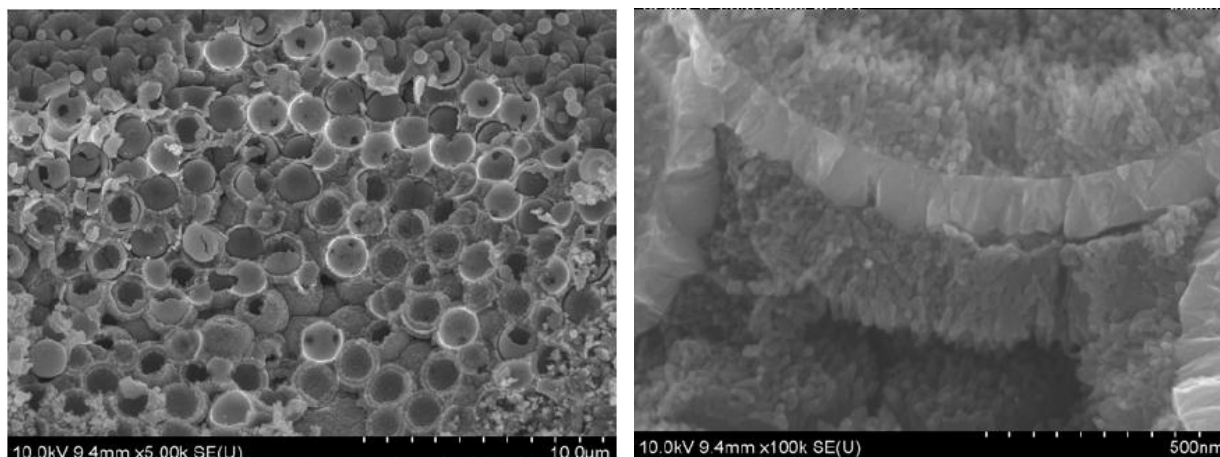


Figure 3.6. The SEM images of the SnO₂ inverse opal structure with mesoporous titania layer deposited on it.

-3 dimensional mesoporous TiO₂/FTO electrode

Deposit Silica particles

Tin Oxide CVD

Etch Tin Oxide

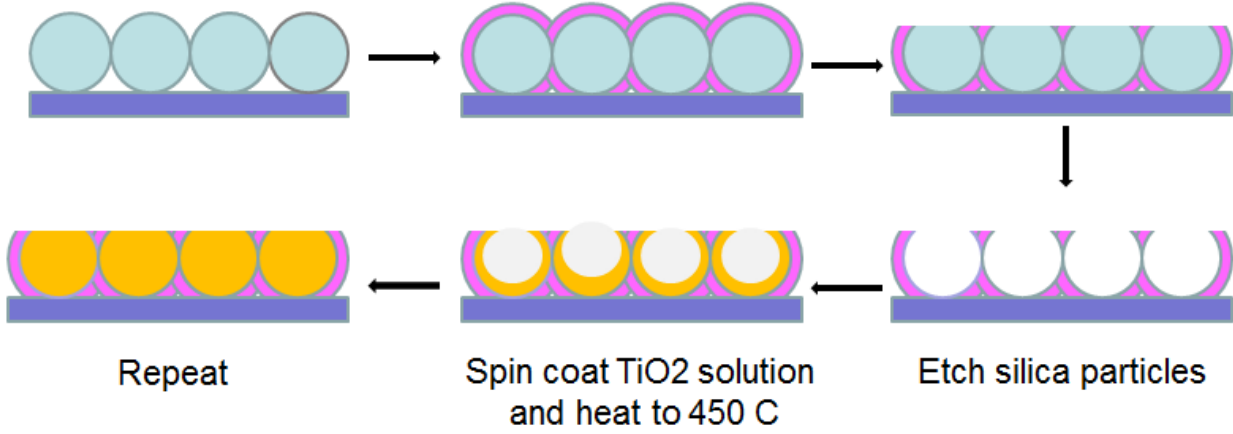


Figure 3.7. The scheme for the fabrication process of 3-D SnO₂ inverse opal structure with mesoporous titania structure.

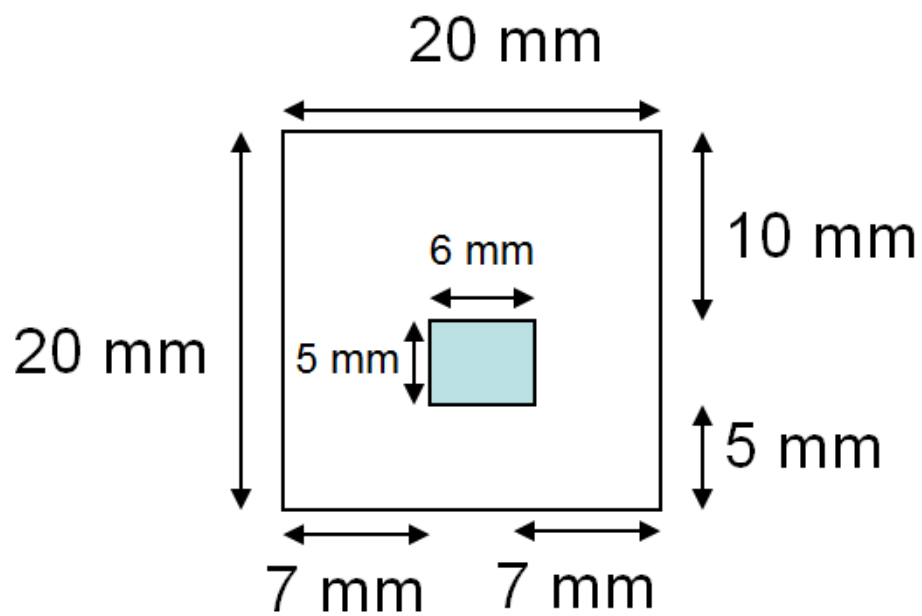


Figure 3.8. The size of the sample cut before sent to Samsung SDI (South Korea).

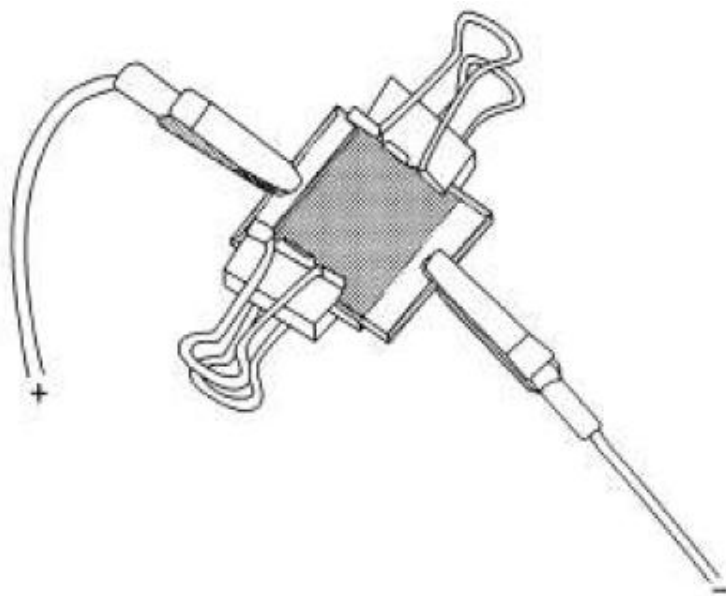


Figure 3.9. The representative illustration of assembled DSSC [10].

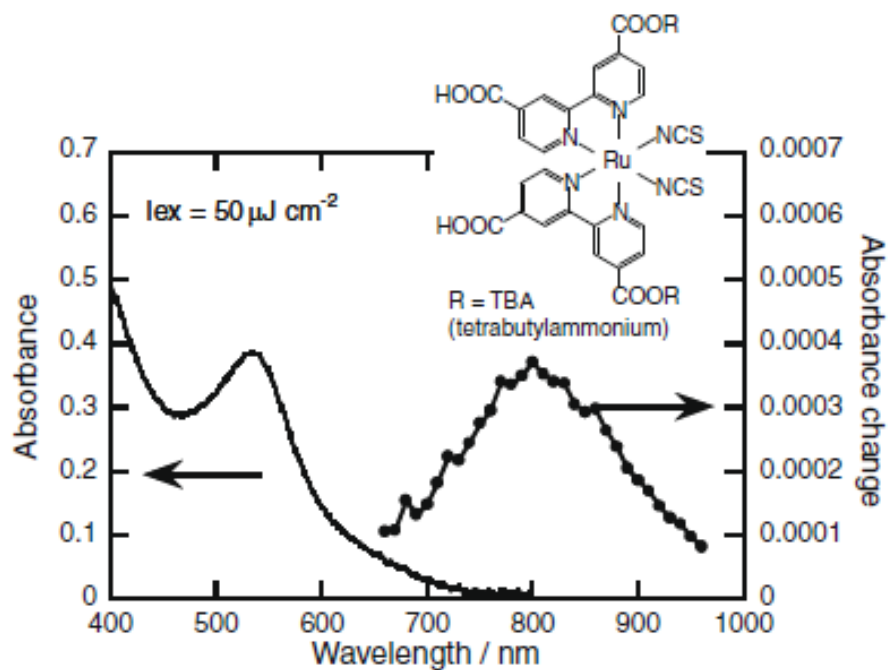


Figure 3.10. The Structure and absorbance of the dye, N719 [13].

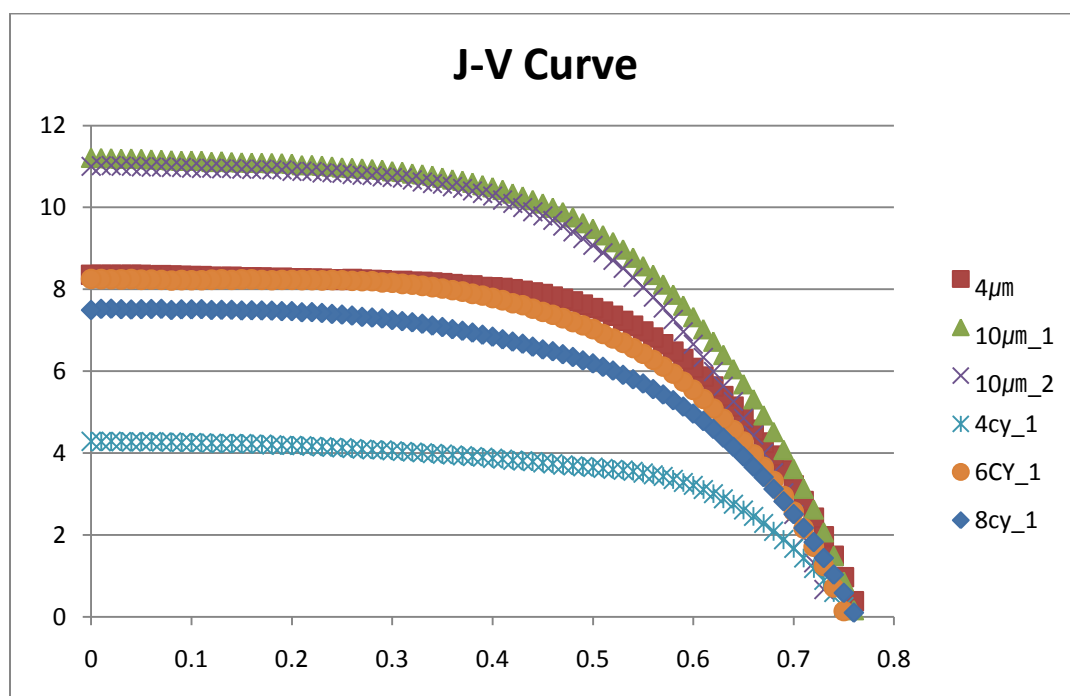


Figure 3.11. The voltage versus current plot for various samples.

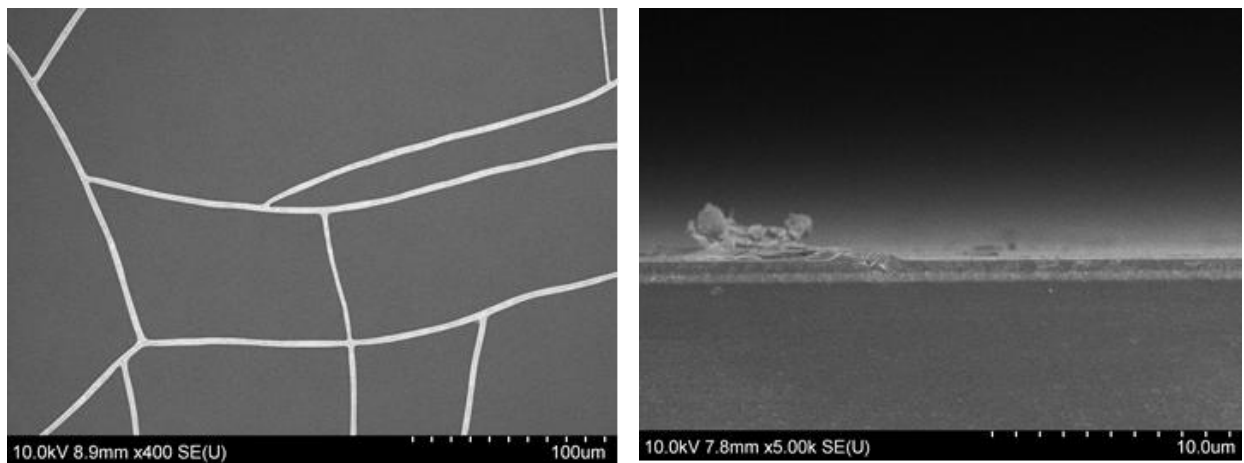


Figure 3.12. The SEM images of the flat titania film.

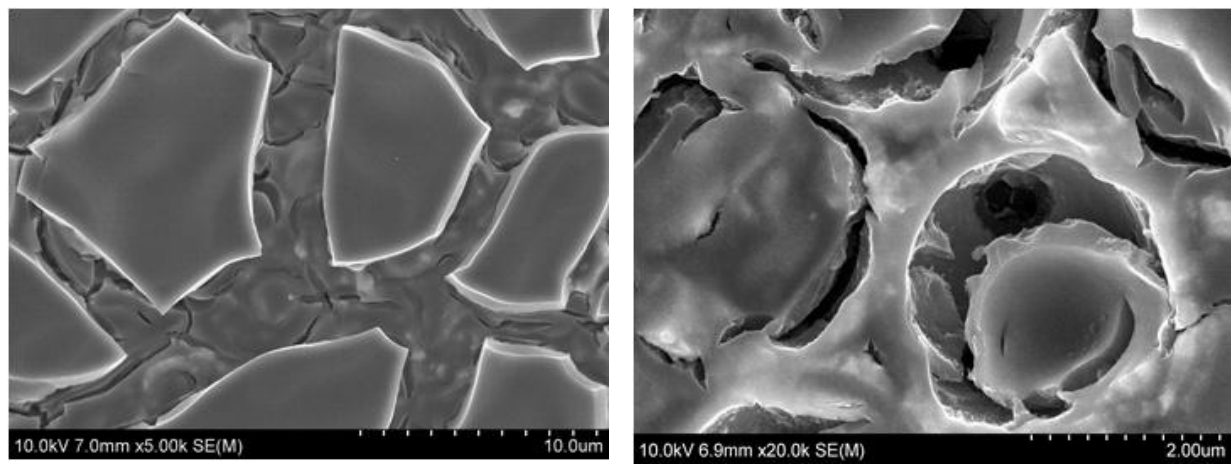


Figure 3.13. The over layer formed on the 3-D Transparent Conductive Oxide DSSC using SnO_2 inverse opal structure along with a titania mesoporous structure.

3.9 References

1. Sterling, V. A. Planning and installing photovoltaic systems: a guide for installers, architects, and engineers; *James & James / Earthcan* **2008**.
2. Palomares, E.; Haque, S. A.; Kroon, J. M.; Durrant, J. R. *J. Phys. Chem. B* **2005**, 109, 12525-12533.
3. O'Regan, B.; Gratzel, M. *Nature* **1991**, 353, 737-739.
4. Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Bessho, T.; Gratzel, M. *Journal of American Chemical Society* **2005**, 127, 16835-16847.
5. Hagfeldt, A.; Gratzel, M. *Accounts of Chemical Research* **2000**, 33, 269-277.
6. Yoon, C.H.; Vittal, R.; Lee, J.; Chae, W.S.; Kim, K.J. *Electrochimica Acta* **2008**, 53, 2890-2896.
7. Hauch, A.; Georg, A. *Electrochimica Acta* **2001**; 46; 3457-3466.
8. Gratzel, M. *Pure Applied Chemistry* **2001**, 73, 459-467.
9. Nazeeruddin, M.K.; Kay, A.; Rodicio, I.; Baker, R.H.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *Journal of American Chemical Society* **1993**, 115, 6382-6390.
10. Smestad, G.P. *Solar Energy Materials and Solar Cells* **1998**; 55; 157-178.
11. Tennakone, K.; Kumarasinghe, A.R., Kumara, G.R.R.A., Wijayantha, K.G.U.; Sirimanne, P. M. *Semiconductor Science Technology* **1995**; 10; 1689-1693.
12. Gratzel, M. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**; 164; 3-14.
13. Katoh, R.; Kasuya, M.; Furube, A.; Fuke, N.; Koide, N.; Han, L. *Chem. Phys. Lett.* **2009**, 471, 4-6, 280-282.

CHAPTER 4

Conclusions

This thesis focuses on the various applications of 3-D inverse opal microstructures. In order to fabricate this 3-D microstructure, we use colloidal self-assembly to prepare the basic structure explained in chapter 1. Understanding the forces and interactions of these colloidal particles are important in order to generate a designed 3-D colloidal structure. We mainly use vertical deposition (Figure 1.5).

In chapter 2, the conductive substrate is patterned first. Then the colloidal crystal is grown on the entire surface. To the colloidal crystal grown substrate, nickel is deposited by electro deposition. After removing all the colloidal particles, we form a 3-D nickel inverse opal microstructure. With this method, the nickel inverse opal cantilever is prepared (Figure 2.1). Since it is fairly easy to generate layered microstructure using this approach, 3-D copper inverse opal microstructure and 3-D gold/nickel bilayer inverse opal microstructure has been made (Figure 4 and Figure 10). These devices have unique optical, thermal and mechanical properties and can be used as actuators and chemical sensors. The mechanical properties of these cantilevers are shown in Figure 2.7 and Figure 2.9.

Also we demonstrated that we can fabricate 3-D transparent conductive oxide DSSC with SnO_2 inverse opal structure and mesoporous titania structure (Figure 3.6). The SnO_2 inverse opal structure is formed by using CVD and the mesoporous titania layer is formed inside this inverse structure through solution dipping approach. However, the over layer on top of the surface prevents more titania layer to infill the inverse structure (Figure 3.13). The data plots shown in table 3.1 make sense, but there are still more data in order to prove that the inverse opal structure

along with the mesoporous structure as mentioned in chapter 3. Also more data is needed to prove that using larger silica particles will have advantage over using smaller silica particles.

AUTHOR'S BIOGRAPHY

Tae Wan Kim was born in Seoul, South Korea on December 17, 1986. He attended the University of Illinois at Urbana-Champaign and earned his Bachelor of Science in Chemistry in 2005. He participated in summer internship, which includes working at Han Yang University (South Korea) in 2006, Kumkang Korea Chemicals Company (South Korea) in 2007, and Autonomic materials INC. (Champaign, IL) in 2009. He began his graduate studies at University of Illinois at Urbana-Champaign in Material Science and Engineering in 2005 under the instruction of Professor Paul Braun. Tae Wan's research focused on fabrication and characterization of nanostructures along with the fabrication of DSSC. Tae Wan graduated from the University of Illinois at Urbana-Champaign in 2011 and went to KAIST University (South Korea) to continue his PhD program.