

Investigate Novel Inkjet Printing of High Performance Silica-based Nanostructured Anti-Reflection Coatings

by
Harrison Robert Holzgang

A PROJECT

submitted to
Oregon State University
University Honors College

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the requirements for the
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Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

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Harrison Robert Holzgang for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on May 28th, 2015. Title: Investigation of Novel Inkjet Printing of High Performance Silica-based Nanostructured Anti-Reflection Coatings.

Abstract approved: _____

Chih-Hung Chang

Anti-reflective coatings are applied to substrates to increase the transmittance of light in the visible range of wavelength 400 – 800 nm through the substrate by changing the refractive index at the surface and directing more light through the substrate rather than being reflected away. This project investigated the possibility of applying a coating made from silica nanoparticles through an inkjet printer as opposed to dip-coating and spin-coating methods that are already used. Applying the coating from a printer will enable the ability to print directly onto items with various shapes like a phone screen and eye glasses and reduce glare on the screen or lens. A uniform coating onto glass and silicon wafer substrates was achievable. Experiments showed that print coating of solid and hollow silica films could increase the transmittance of light by 3% or more. The silica coating had moderate mechanical resistance that is a point for further improvement. The process of print coating the silica nanoparticles had a tendency to clog ink cartridges but cautious care eventually showed that this complication was avoidable. Print coating of anti-reflective silica nanoparticles is a feasible process.

Key Words: Anti-Reflective Coatings, Silica Nanoparticles, Hollow Silica Nanoparticles, Inkjet Printing

Corresponding e-mail address: holzgangh@gmail.com

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APPROVED:

Chih-Hung Chang, Mentor, representing Chemical Biological & Environmental Engineering

Greg Herman, Committee Member, representing Chemical Biological & Environmental Engineering

Changho Choi, Committee Member, representing Chemical Biological & Environmental Engineering

Toni Doolen, Dean, University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

Harrison Robert Holzgang, Author

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Table of Contents

1. Introduction	1
2. Background	2
2.1 Anti Reflectance	2
2.2 Silica Nanoparticle Coatings Techniques	3
2.3 Inkjet Printing.....	3
3. Experiment.....	5
3.1 Experimental Overview.....	5
3.2 Synthesis of solid silica nanoparticles.....	5
3.3 Synthesis of hollow silica nanoparticles.....	5
3.4 Ink development	6
3.5 Substrate preparation.....	6
3.6 Printing.....	7
3.7 Substrate Testing and Characterization.....	7
4. Results	9
4.1 Light Transmittance from Inkjet Printed Films Based on Solid Silica NPs.....	9
4.2 Light Transmittance from Inkjet Printed Films Based on Hollow Silica NPs	11
4.3 Mechanical resistance of Solid and Hollow Silica NPs	13
.....	15
4.4 Resolution of Print Coating Deposition Technique.....	15
5. Discussion.....	16
5.1 Ink Development (Table 1).....	16
5.2 Total Light Transmittance of Anti-Reflective Films	16
5.3 Mechanical Resistance of Anti-Reflective Films	17
5.4 Resolution of Anti-Reflective Films	18
5.5 Clogging of Ink Cartridge for Inkjet Printer	18
6. Conclusion.....	20
Bibliography	21
Appendix 1. SEM Imaging	22
Appendix 2. Total Light Transmittance Data.....	26

A2.1 Solid Silica	26
A2.2 Transmittance and MRT Data for Hollow silica samples	28
Appendix 3. Imaging of Inkjet Printer System	30

List of Figures

Figure 4.1: Total light transmittance of single layer solid silica coating.....	9
Figure 4.2: Change in total light transmittance for single layer solid silica coating	9
Figure 4.3: Imaging of single layer solid silica coating	10
Figure 4.4: Total light transmittance of 3 layer solid silica coating	10
Figure 4.5: Change in total light transmittance of 3 layer solid silica coating.	11
Figure 4.6: SEM imaging of 3 layer solid silica coating.	11
Figure 4.7: Total light transmittance of 5 layer hollow silica coating.	12
Figure 4.8: Change in total light transmittance of 5 layer hollow silica coating	12
Figure 4.9: SEM imaging of 5 layer hollow silica coating	13
Figure 4.10: Total light transmittance of solid silica coating before and after MRT	14
Figure 4.11: Difference in light transmittance of solid silica before and after MRT	14
Figure 4.12: Total light transmittance of hollow silica coating before and after MRT	14
Figure 4.13: Difference in light transmittance of hollow silica before and after MRT	15
Figure 4.14: Imaging of print coating resolution	15
Figure A1.1: SEM Image of hollow silica nanoparticles.....	22
Figure A1.2: SEM image of single layer solid silica coating	23
Figure A1.3: SEM image of single layer solid silica coating print induced pattern.....	24
Figure A1.4: SEM image of hollow silica coating	25
Figure A2.1: Total light transmittance of 3 layer solid silica coating replicate I	26
Figure A2.2: Change in light transmittance of solid silica with bare glass and MRT I.....	26
Figure A2.3: Total light transmittance of 3 layer solid silica coating replicate II.....	27
Figure A2.4: Change in light transmittance of solid silica with bare glass and MRT II ...	27
Figure A2.5: Total light transmittance of 5 layer hollow silica coating replicate I.....	28
Figure A2.6: Change in light transmittance of hollow silica to bare glass and MRT I	28
Figure A2.7: Total light transmittance of 5 layer hollow silica coating replicate II.....	29
Figure A2.8: Change in light transmittance of hollow silica to bare glass and MRT II....	29
Figure A3.1: Image of the DMP-2831 Printer used for experiment under a hood.	30
Figure A3.2: Imaging of ink cartridge head	31
Figure A3.3: Imaging of ink cartridge inside printer	31
Figure A3.4: SEM image of ink cartridge nozzle	32
Figure A3.5: SEM image of clogged ink cartridge nozzle	32

List of Tables

Table 3.1: Ink Recipes	6
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1. Introduction

Anti-reflective coatings are used to increase the transmittance of light by shifts in the index of refraction. Their uses are numerous. Most glass reflects about 8% of the visible light that shines on to it. Anti-reflective coatings can drastically decrease the reflectance. Coatings can be used to coat the glass surface of solar cells to improve the overall efficiency by simply getting more photons into the actual solar cell itself. The coating can also be applied to optical devices like a pair of glasses or windows reducing the glare. Another possible application is to put the coating onto the screen of electrical devices such as a phone and reduce the glare that makes the screen difficult to read while outside.

Current methods of applying anti-reflective coatings are spin coating and dip coating. These methods are effective for gaining a consistent film across an entire surface but lack the ability to pattern around unique feature like a speaker. By print coating the film instead it is possible to avoid features on a screen where the coating would be undesirable or create patterns on the device. Print coating would also make it possible to apply the coating on devices post market. The objective of this project is to investigate the feasibility of using an ink jet printer to apply anti-reflective coatings.

2. Background

2.1 Anti Reflectance

The basis for anti-reflectance is the index of refraction¹. The path that light is traveling bends when the medium through which it is traveling changes. Different mediums have different indices of refraction. At the surface point of a new medium the light can do one of three things. Light can be absorbed by the medium molecules, the direction of travel can change and the light be transmitted or the light can reflect off the surface. Creating a more gradual shift of refraction index between two surfaces increases the amount of light that refracts through versus reflecting off.

The discoveries of anti-reflective properties were found under the examination of a moth's eye. As a nocturnal insect the moth needs to evolutionarily advantageous to be able to take in as much light as possible and having no light reflect off is also beneficial to avoiding predators. As a result the eye's developed a nano-scale texturing that lowers the effective refractive index. Initial anti-reflective coatings were inspired and designed to imitate the moth eye¹. Anti-reflective properties were used before this discovery but the discovery did lead to methods attempting to recreate the effect through biomimicry of the moth's eye. This is the methodology used in the experiments of this paper.

For typical glass 90-92% of the visible light that comes in contact is transmitted through. Absorption accounts for 0-2% of the contact light and about 8% of the light is reflected off the surfaces². Reflectance of light that is normal to a surface is modeled by Equation 1¹ the Fresnel equation. The Fresnel equation takes into account three variables; the refractive index of air (n_{air}), the substrate (n_s) and the anti-reflective coating (n). This model also assumes that the absorbance of light in the film and substrate are negligible.

$$r = \left(\frac{n_{air}n_s - n^2}{n_{air}n_s + n^2} \right)^2 \quad (1)$$

Setting r equal to zero the optimal refractive index of a film can be solved for. The optimal thickness of an anti-reflective coating for a specific wavelength range can be described by Equation 2¹ and Equation 3¹ where λ_1 and λ_2 are the wavelengths to defining the spectral range, and n is the refractive index of the film and d_c is the film thickness.

$$\lambda_0 = \frac{2\lambda_1\lambda_2}{\lambda_1 + \lambda_2} \quad (2)$$

$$d_c = \frac{\lambda_0}{4n} \quad (3)$$

2.2 Silica Nanoparticle Coatings Techniques

While numerous materials and techniques are used to create anti-reflective properties, the material of focus in this study is silicon dioxide or what is often referred to as silica. The conventional methods of applying the silica nanoparticle film are spin coating and dip coating. Spin coating works by spinning the substrate at a high rpm and dropping a small volume of the solution in the center. The solution is then spread across the substrate due to the centripetal force. For dip coating the substrate is slowly lowered into a solution and then slowly withdrawn back out. The film thickness and uniformity is affected by the rate of withdrawal and the volatility of the solvent⁶. When applied to anti-reflective coatings made of silica nanoparticles (NPs), results have shown for both methods that the reflected lights can be reduced down to 1% or lower⁵.

2.3 Inkjet Printing

Inkjet printing as a deposition technique has many advantages over other common techniques such as spin coating. Due to the ability of being able to deposit a film to a designed pattern, materials can be conserved. Only the material that is required needs to be printed versus the coating of an entire surface and etching off what is undesired. In the case of spin coating the majority of your material is spun off and unused in the process as well. Another advantage is that inkjet printing can easily be applied to large area coating that is not always possible with other methods.

Inkjet printing works by the use of piezoelectric technology⁴. The process starts with a main reservoir filled with a liquid solution that is connected to small micro sized chambers by microchannels. On top of the chamber is a piezoelectric. Piezoelectric materials are crystalline materials whose lattice structure changes dependent on the strength of an applied voltage to the crystal. A small electric signal is sent from the printer to the crystal causing the crystal to morph pushing down on liquid in the chamber and ejecting a droplet out of the chamber. When the voltage to the crystal is ceased the crystal morphs back to its original shape drawing more liquid into the chamber from the ink reservoir.

Surface tension and viscosity become crucial properties to the liquid being used as an ink for an inkjet printer⁴. Inks with very low viscosities and surface tension flow too easily and can flow out of the nozzles due to gravity and head pressure. Even if the surface tension and viscosity are strong enough to stay in place when being held in the chamber a clean droplet may not be obtainable and liquid will squirt out when ejected. Conversely if viscosity is too strong the ink will struggle to flow through microchannels between the

chamber and ink reservoir. When the signal to the piezoelectric is backed off allowing the crystal to relax back to the original form the chamber then pulls in air from the nozzle instead of ink from the reservoir. With the surface tension being too high the piezoelectric can push down on the liquid and form a droplet but the force of surface tension is too strong for gravity to overcome and the droplet is not ejected. The droplet then can be sucked back up or ejected in the next push with more liquid. As a result inks must be developed to fall into a specific range of viscosity and surface tension.

3. Experiment

3.1 Experimental Overview

The experiment started with the synthesis of silica NPs. At the beginning of the research the NPs synthesized were solid spheres of about 40 nm in diameter. Eventually experiments were conducted with hollow sphere particles of the same approximate size. The silica NPs were then mixed with a binding solution and ethylene glycol to create a suitable ink to be used in the printer. The ink was then printed on in a block pattern to coat glass and silicon wafer substrates. Printing on silicon wafers with oxidized surface was done for easy examination of the film for undesirable patterning by the naked eye and by scanning electron microscopy. Glass substrates were tested for their transmission of light by UV-vis spectroscopy. The mechanical resistance of the film was tested by scratch of the film followed by retesting the light transmission and looking for significant shifts in the amount of light transmitted through the entire substrate.

3.2 Synthesis of solid silica nanoparticles

The base for the silica particles used was tetraethyl orthosilicate (TEOS) and was carried in an ethanol solvent. Synthesis was completed by first adding 1 ml of deionized water into 49.5 ml of 200 proof ethyl alcohol inside an Erlenmeyer flask. 2.23 ml of TEOS and 1 ml of NH_3OH were then added into the solution in the respective order. The flask was sealed by Parafilm and allowed to react for at least 10 hours being stirred by a magnetic stir rod. When the reaction was finished a sample from the solution was taken and mixed with ethanol in a 10:1 dilution. The diluted sample was then used to confirm the particle size by dynamic light scattering (DLS). If the average particle size was less than 30 nm or greater than 50 nm the solution was not used for print coating.

3.3 Synthesis of hollow silica nanoparticles

Hollow silica particles were synthesized by a fed batch reaction. 0.12 g of polyacrylic acid (PAA) was dissolved into 15 ml of NH_3OH . The resultant solution was then mixed into 30 ml of 200 proof ethyl alcohol. In a separate bottle 0.75 ml of TEOS was mixed into 10 ml of ethanol. A positive displacement micro pump was used on the lowest setting with a 1 mm inside diameter tube to feed the TEOS solution into the PAA solution while being stirred. The solution stirred for 5 hours while the reaction took place around the PAA precursor. After the reaction was finished the PAA and silica was separated by centrifuging the solution leaving hollow spheres of silica NPs.

3.4 Ink development

Both the viscosity and surface tension of the nanoparticle solutions had to be increased for use in the ink jet printer to create a clean and consistent droplet. Ethylene glycol was used to increase both properties. For initial experiments and developed inks, the viscosity and surface tension of the ink were measured. A glass viscometer was used for the viscosity measurement. For the surface tension a Du Noüy ring tensiometer was used. After numerous cycles it was determined that an ink containing approximately 20% ethylene glycol by volume was satisfactory for printing.

In later trials it became standard to evaporate some of the ethanol in the nanoparticle solution off to increase particle concentration. The evaporation was performed under a hood and raising the solution to 80 C. after the solution cooled down to room temperature the density was checked with a goal density to be 0.81g/ml.

To increase the mechanical resistance of the film a binding solution was also added. The binding solution was made by mixing 0.5 ml of 0.1 M HCl and 1 ml of TEOS into 20 ml of isopropyl alcohol (IPA). The ratio of binder added was experimented with in range from 10 -30% volume in the ink. The ideal goal was to use the least amount of binder while providing suitable mechanical resistance. Table 1 shows common ink recipes used for printing.

Table 1: Recipe for inks developed and used to print samples. Data presented in the results section were printed with Ink IV and Ink VII. Only difference between the two inks was the use of solid silica for Ink IV and hollow silica for Ink VII.

Ink	Solid Silica Nanoparticle solution (ml)	Hollow Silica Nanoparticle solution (ml)	Binder solution (ml)	Ethylene Glycol (ml)	Ethanol (ml)
Ink I	1.50	0.00	0.625	1.00	1.00
Ink II	1.25	0.00	0.500	0.60	0.85
Ink III	2.00	0.00	0.500	0.63	0.00
Ink IV	2.00*	0.00	0.500	0.63	0.00
Ink V	2.00*	0.00	0.850	0.50	0.00
Ink VI	0.00	2.00	0.000	0.50	0.00
Ink VII	0.00	2.00	0.250	0.50	0.00

*Ethanol solvent partially evaporated out of solution

3.5 Substrate preparation

Glass and silicon wafers were used as substrates to print on and were prepared identically. The glass used was 1 mm thick glass slides for microscopy. The silicon wafers used had been oxidized so that the surface behaved similarly to the amorphous glass surface than the crystalline surface of pure silicon. The glass slides and wafers were cut into 0.5 in to 1 in squares and sonicated in a 1 M NaOH solution for 4 min. This was done to make the surface more hydrophilic. The substrates were then cleaned by rinsing with acetone and then IPA. Substrates then were blow dried with nitrogen gas.

3.6 Printing

A Dimatix Materials Printer (DMP) 2831 was used for the printing experiment. The printer allows for control of patterning, surface temperature, spacing between droplets and the number of layers to be print. Pictures of the printing system can be found in Appendix 3. Print cartridges had 16 nozzles on the print head. A simple block pattern as used to coat the entire substrate. The printing plate was also heated to 60 C to assist the evaporation of the solvent during the printing process.

Control was given to use any number of the nozzles desired so long as the nozzles in use were adjacent to each other. For all experiments done only 3 nozzles were used but which three were used varied. Control was also given to the voltage and waveform of the signal sent to each nozzle allowing for the adjustment of drop velocity and droplet shape. To reduce the variables in printing a single waveform pattern was used. This pattern is included in Appendix 3 The voltage if the signal sent to the nozzles was aimed for 16 mV but slightly adjusted for each nozzle day to day to maintain consistent drop velocity across all nozzles during printing.

The main parameters experimented with for printing was the ink composition, drop spacing and print layers. The drop spacing is the linear distance between the center of one droplet and the center of all adjacent droplets on the substrate. Drop spacing between 25 and 55 μm were utilized initially. Eventually the experimental range was reduced to be between 30 and 40 μm . Early experiments were only conducted with 1 layer. For experiments with multilayer printing there was a 120 s delay of printing between each layer.

3.7 Substrate Testing and Characterization

After printing substrates were first baked in a furnace at 300 °C for 30 min to cure the silica coating by evaporation of all solvents. Afterwards the glass substrates were tested by shining a full spectrum of visible light through the sample and measuring the transmittance of the light. Initially this test was conducted with an Ocean Optics USB2000 spectrometer and Mikropack light source. A Jasco V-670 spectrometer was also used later on for a more accurate reading with better signal to noise ratio.

The mechanical resistance of the film was tested by agitating the film with a home-made system. The system included a staging center that held and moved the substrate under a dense pad for 100 cycles. The pad was held in place with a metal rod and weighed down with a 500 g weight. After the film had been agitated it the substrate was rinsed with deionized water and baked again. The substrate's light transmittance was retested and compared to the transmittance completed before the mechanical resistance test. To quantify the mechanical resistance a relative change in transmittance (RCT) was defined and used and calculated by Equation 4. T is the transmittance. For one sample the difference between the transmittance before and after the mechanical resistance test at a

given wavelength was found. This value was then divided by the difference in transmittance between the sample before the resistance test and the bare glass at the same wavelength. This was then done at every wavelength in the visible spectrum and an average value was taken and converted into a percent.

$$(RCT) = 100 \left[\frac{T_{PostMRT} - T_{PreMRT}}{T_{PreMRT} - T_{BareMRT}} \right] \quad 4$$

4. Results

4.1 Light Transmittance from Inkjet Printed Films Based on Solid Silica NPs

Single layer printing of solid silica NPs showed increases in transmittance from bare glass but was unable to obtain comparable results to other deposition methods. Figure 4.1 and 4.2 shows the top results from single layer printing of solid silica. The film simply was not reaching the thickness needed for high transmittance. The only control on film thickness was drop spacing. The minimum drop spacing capable of the system was 30 μm . Decreasing the drop spacing further led to the droplets forming into one big mass. After drying the film showed patterns similar to streaking and tear drops. It is suspected that this patterning may have resulted from natural convection and the marangoni effect while the solvent was evaporated off. Figure 4.3 is pictures of the film printed onto silicon wafers.

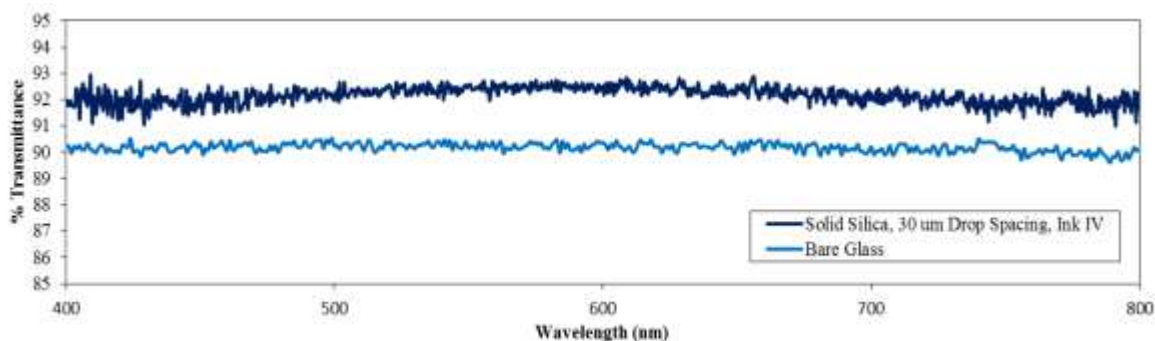


Figure 4.1: Transmittance data for single layer coating of solid silica film printed with 40 μm drop spacing compared to transmission for the bare glass. Data is of the best results obtained for single layer printing with solid silica NPs. The average transmission across all wavelengths for sample was 92.1% while the average for the bare glass was 90%. More data is provided in Appendix.

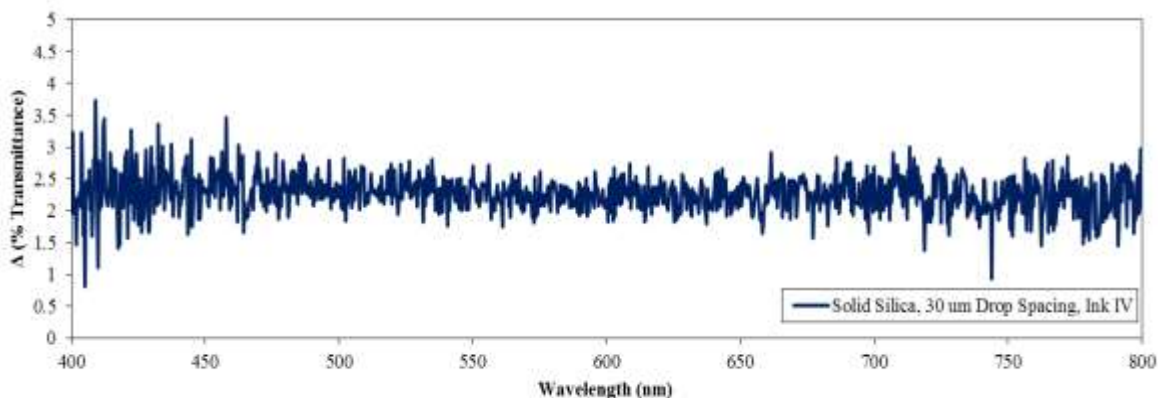


Figure 4.2: Change in transmittance from bare glass to a single layer of solid silica coating printed at 40 μm drop spacing. Data is from the sample in Figure 1:

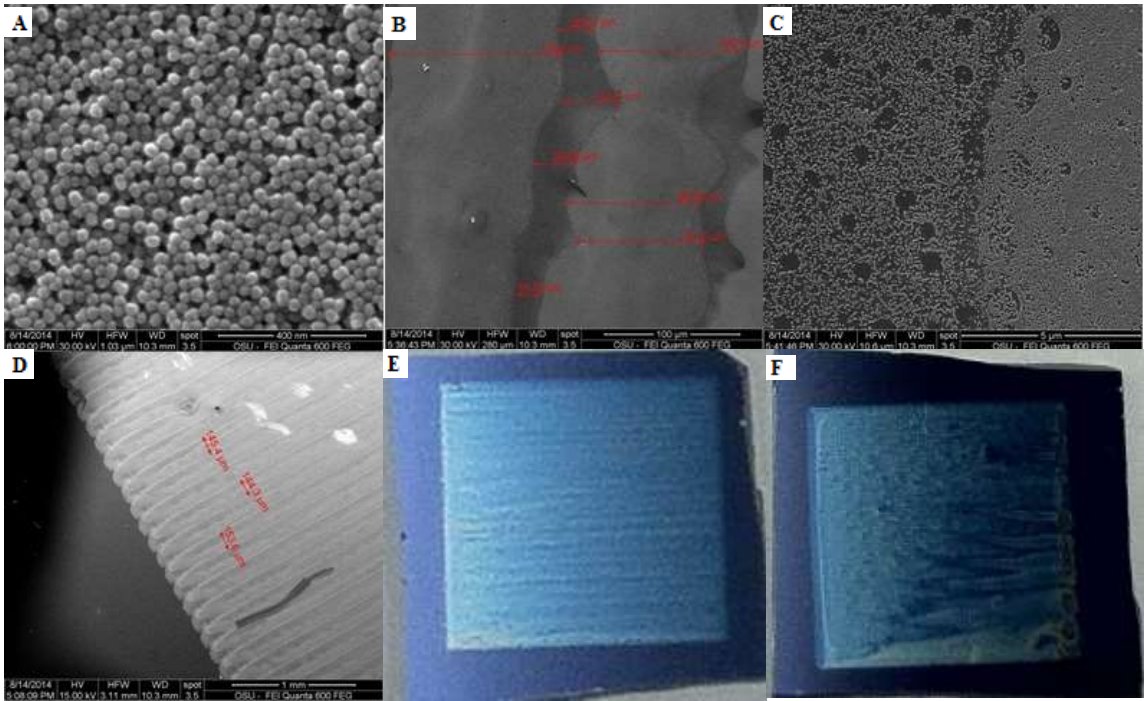


Figure 4.3: (A) SEM image of solid silica print coated onto sample. (B) SEM image of line pattern created from print coating. (C) SEM image zoomed in near edge of block pattern. (D) SEM of coated sample viewing lines and edge of block pattern. (E) Photograph of solid silica printed at 50 μm drop spacing. Lines induced by printing. (F) Photograph of solid silica printed at 30 μm drop spacing where patter distortion occurred.

Multiple layer printing and surface heating were introduced into the experiment. 3 cycle printing at 35 μm drop spacing yielded top results and closest competitor to other deposition methods. Heating of the surface allowed for faster evaporation of solvent and allowed for smaller drop spacing without pattern distortion. Figure 4.4 presents transmittance data for samples taken on the Jasco spectrometer. Figure 4.5 shows the difference in light transmittance from the bare glass to the coated sample. Figure 4.6 presents SEM imaging of the sample.

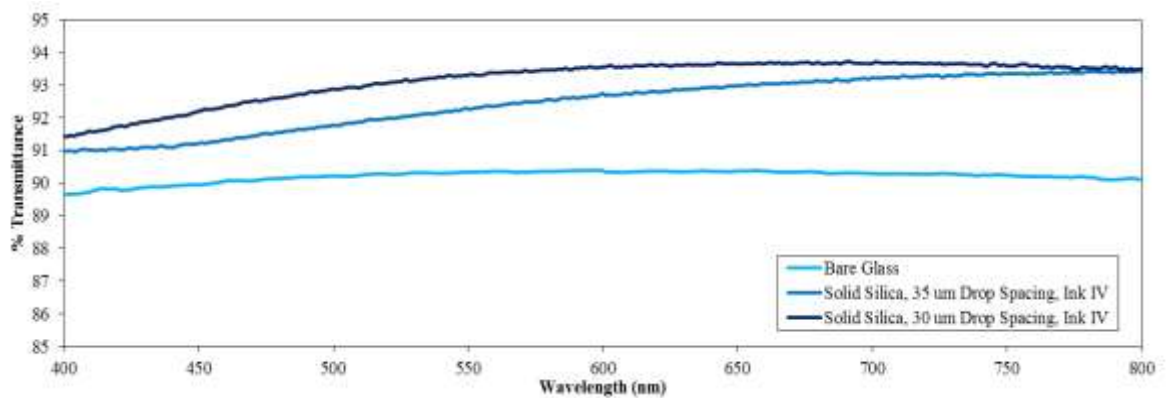


Figure 4.4: Transmittance data for solid silica print coated with three layers onto glass with drop spacing of 30 μm and 35 μm .

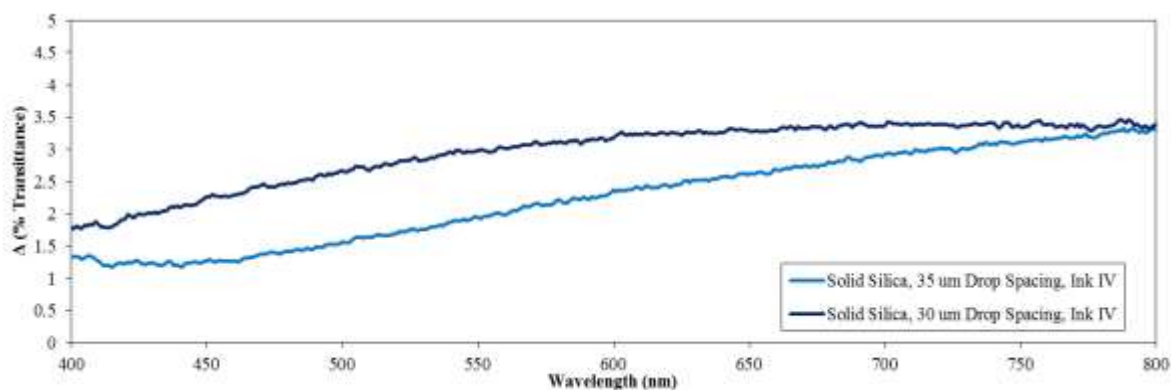


Figure 4.5: Change in light transmittance across the visible spectrum between bare glass and coated samples. Total light transmittance of samples is shown in Figure 4.4.

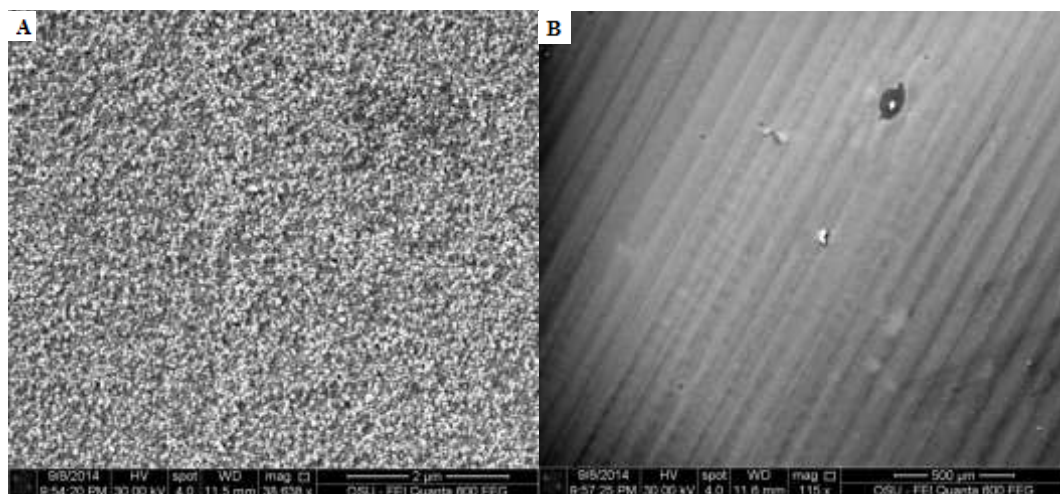


Figure 4.6: SEM imaging of with 3 layers of print coated solid silica particles and drop spacing of 35 μm . (A) Image of particles showing density of film increased from single layer printing. (B) Image of lines induced from printing.

4.2 Light Transmittance from Inkjet Printed Films Based on Hollow Silica NPs

Hollow silica has been printed with drop spacing of 30 and 35 μm with the best results being yielded at the 30 μm level. Issues with consistent printing have persisted with printing hollow silica particles. Film thickness and coverage has not been satisfactory even when printing 5 layers (See Figure 4.6B). The transmission has resulted in a peak around 92.5% only slightly better than the transmittance of the single layer of solid silica. As well it appears that PAA still present in the film affects the transmittance. Increasing the temperature and time that the sample is baked after printing has helped increase the transmittance of light through the substrate. Figure 4.7 shows transmittance data of a sample coated with hollow silica and Figure 4.8 shows the difference in light

transmittance of the samples and bare glass. The drop spacing for the sample was 30 μm and 5 layers were printed on. The sample was first baked for 30 min at 300 $^{\circ}\text{C}$. After the transmittance was tested the sample was baked again for an additional 30 min at 350 $^{\circ}\text{C}$ and retested. Figure 4.9 shows SEM imaging of sample printed under the same conditions.

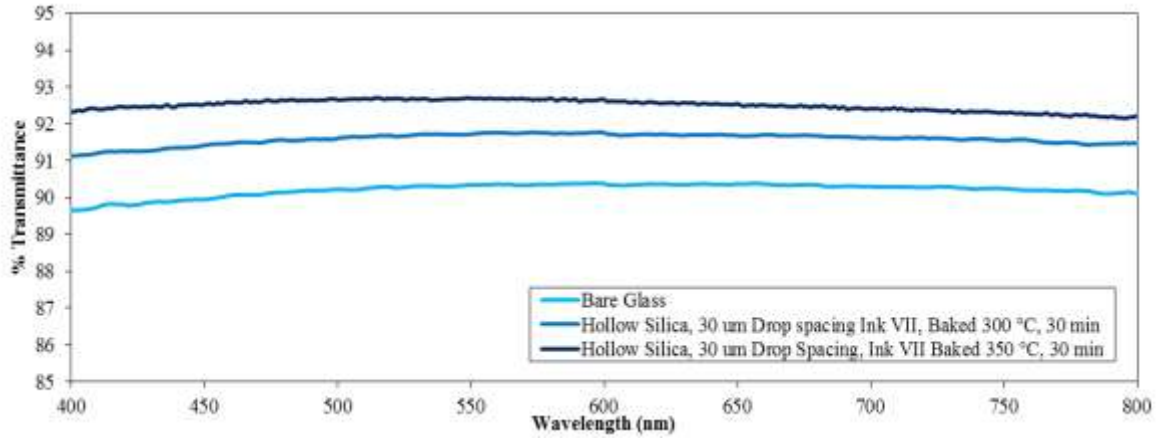


Figure 4.7: Transmittance data for sample coated with 5 layers of print coated hollow silica particles. Sample was baked for 30 min at 300 $^{\circ}\text{C}$ and tested. After testing the sample was baked again for additional 30 min at 350 $^{\circ}\text{C}$ and then had transmittance retested.

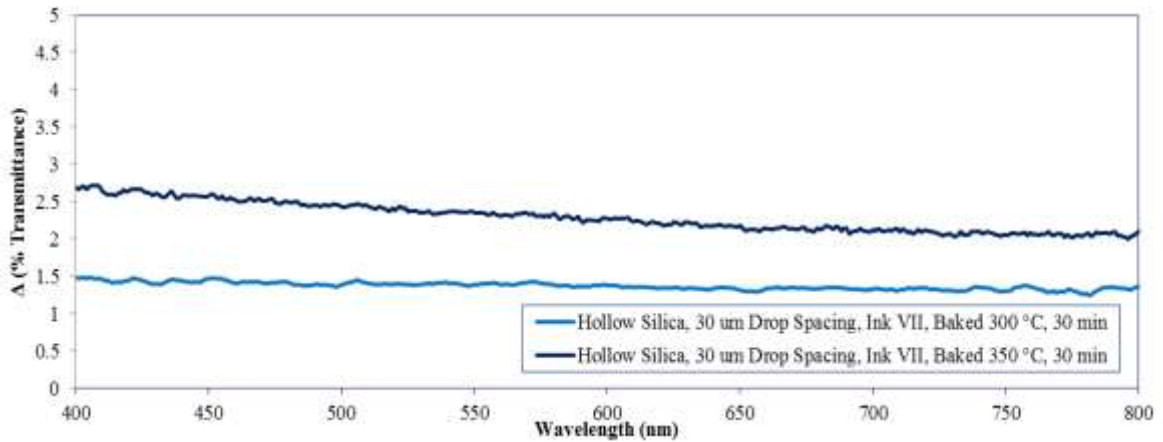


Figure 4.8: Change in light transmittance across the visible spectrum between bare glass and coated samples. Total light transmittance of samples is shown in Figure 4.7.

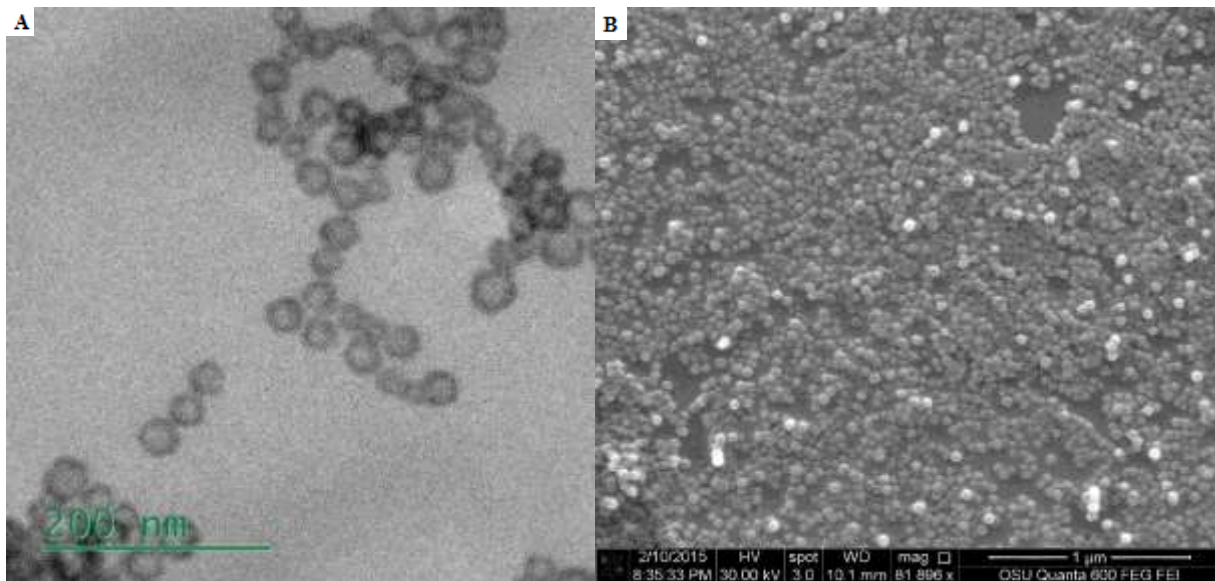


Figure 4.9: (A) TEM image of hollow silica particles, providing scale for an approximate size. (B) SEM image of sample printed with 5 coats of hollow silica at 30 μm drop spacing. Particles do not fully cover substrate and vary in density.

4.3 Mechanical resistance of Solid and Hollow Silica NPs

Initial mechanical resistance without baking (curing) showed the film to have no resistance to mechanical tests at all. Once the baking of samples after printing was introduced mechanical resistance became apparent. Figure 4.10 presents the mechanical resistance data for the solid silica sample printed with 35 μm drop spacing. Figure 4.11 shows the difference in light transmittance of the sample before and after the mechanical resistance test.

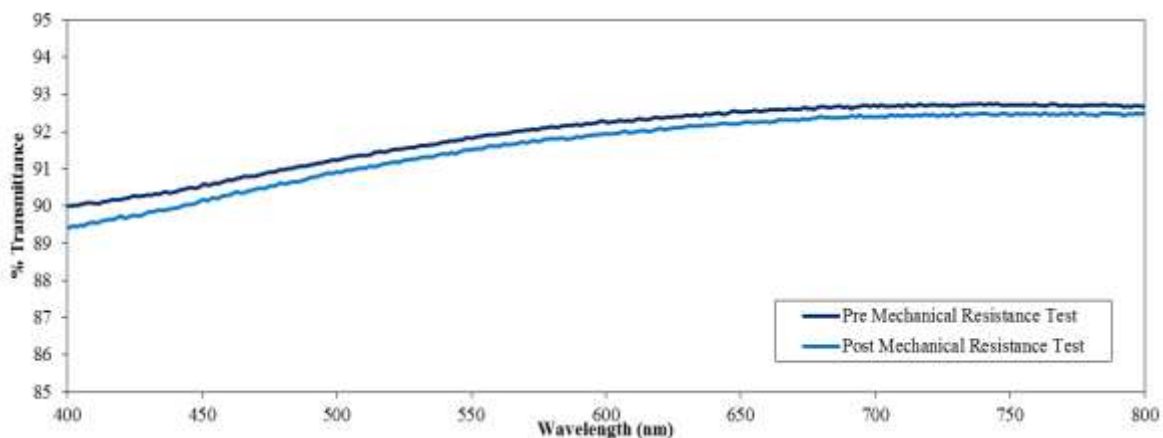


Figure 4.10: Transmittance data of sample with 3 print coatings of solid silica, Ink IV at 35 μm drop spacing before and after a mechanical resistance test. Relative drop in increased transmittance averaged across entire visible spectrum was 33%.

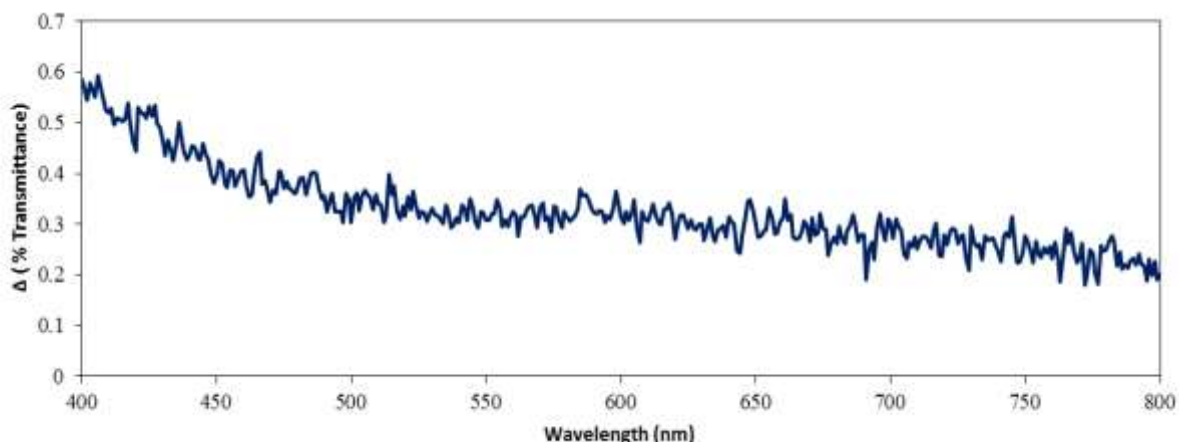


Figure 4.11: Change in total light transmittance across the visible spectrum of sample before and after mechanical resistance test. Sample print coated with 3 layers of solid silica NPs at 35 μm drop spacing.

Figure 4.12 presents mechanical resistance data for a sample printed with 6 layers of a hollow silica sample. While the transmittance relative to bare glass was only a slight increase the mechanical resistance was very strong. The main significance of this result is that it suggests that adequate mechanical resistance is obtainable. The relative change in increased transmission across the visible spectrum is 12.4%. Figure 4.13 shows the difference in light transmittance before and after the mechanical resistance test.

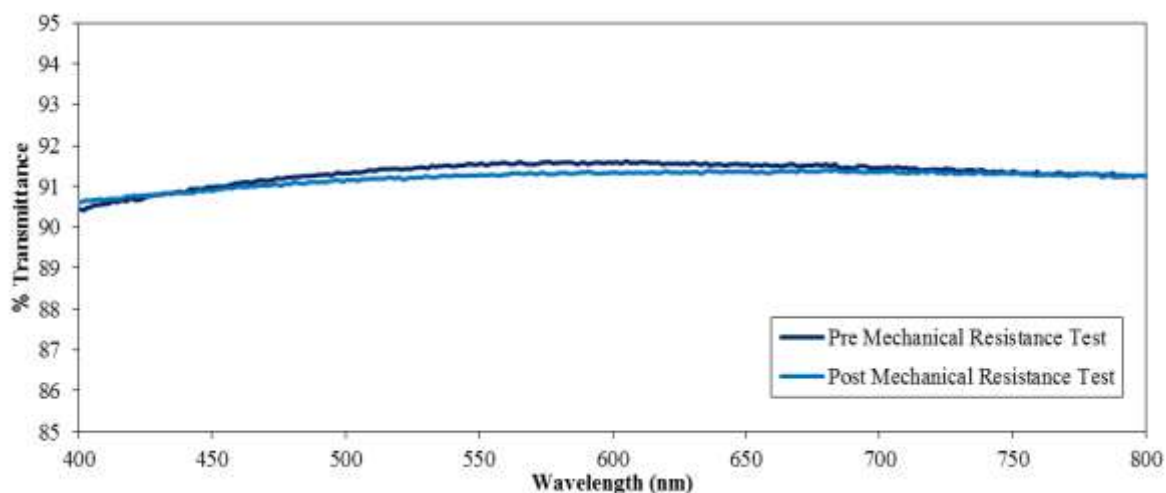


Figure 4.12: Transmittance data for sample with 6 layers of print coated hollow silica, Ink VI and based at 350 $^{\circ}\text{C}$ for 30 min that underwent a mechanical resistance test.

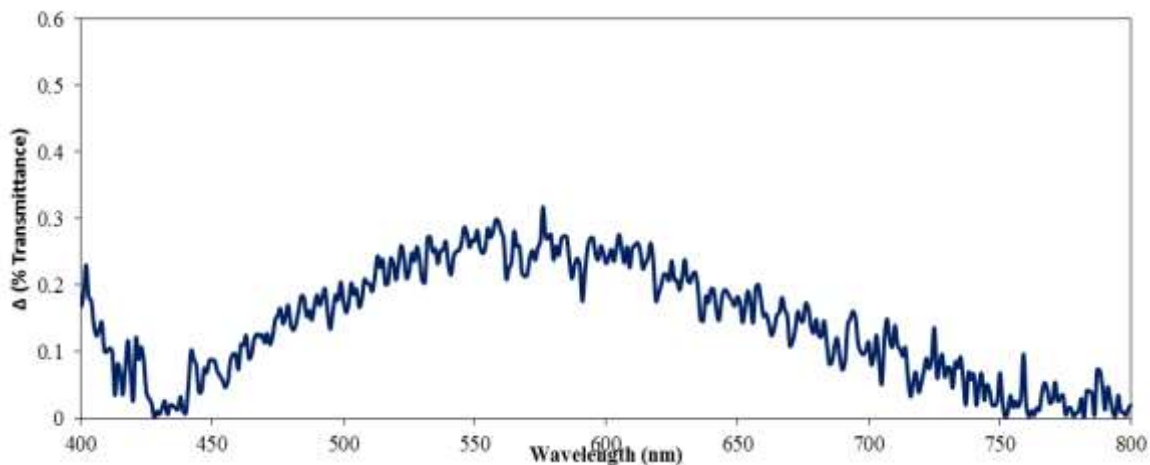


Figure 4.13: Change in total light transmittance across the visible spectrum of sample before and after mechanical resistance test. Sample print coated with 6 layers of hollow silica NPs at 30 μm drop spacing.

4.4 Resolution of Print Coating Deposition Technique

A final aspect examined in the study was the resolution at which the film can be printed. One advantage to printing is the capability to impart a pattern directly onto the substrate. Printing 5 layers of hollow silica with 30 μm drop spacing in an OSU pattern was performed as a simple method to examine the resolution of the film. Figure 4.9 shows imaging of the sample.

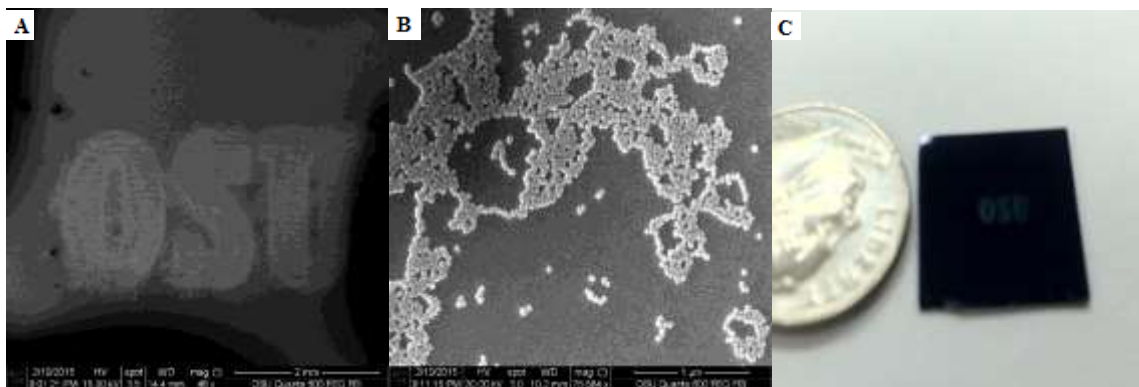


Figure 4.14: (A) SEM image the entire “OSU” pattern. (B) SEM image of particles near sitting outside of defined “OSU” pattern. (C) Image of the sample next to an American dime for relative size.

5. Discussion

5.1 Ink Development (Table 1)

For Ink I and Ink II, ethanol was added to the solution further diluting the NPs. The ink printed fine but the film appeared faint on the substrate and was hardly discernable. The first significant change in the ink development was to increase the particle concentration by no longer adding extra ethanol into the ink. This third ink was used in printing a single layer of solid silica particles and while the light transmittance performance and film uniformity improved it still was not strong enough. At this point in time no mechanical resistance tests were being performed since the sample transmittance had not been very high. To further improve the film thickness the next step was to increase particle concentration again by evaporating ethanol out of the silica nanoparticle solutions before mixing with the binder and ethylene glycol. The increased transmittance still was low but a mechanical resistance test was run out of curiosity. The small amount of film that had been present wiped clean off. The percent of binder added into Ink V from Ink IV was increased due to the results from the mechanical resistance test. Unfortunately this increase in the binding solution led to very rapid clogging of ink cartridges. At this point in the experiment, it was determined a single layer of print coating was not going to obtain high transmittance. Focus of the experiment moved away from optimizing the ink and towards printing multiple layers with the current recipe Ink IV. Eventually a switch to experimenting with hollow silica NPs was made but the same ratios of particle solution, binder and ethylene glycol was used (Ink VII).

5.2 Total Light Transmittance of Anti-Reflective Films

Glass transmits around 90-92% of the light in the visible spectrum of 400 – 800 nm that comes into contact with its surface. 0-2% is generally absorbed and around 8% is reflected between both sides. Anti-reflective coatings can help increase the transmittance by up to 4% per side. A suitable coating will increase transmittance by at least 3% per side or 6% total.

For the solid silica coatings printed the vast majority of samples were single layer prints and did not obtain transmittance above a 3% increase. After trying to improve the film thickness by improving the particle concentration and having little success, it was time for a new solution. Looking into the printer manual further it was discovered that the number of layers printed could be increased. An attempt at two layers and then 3 layers

was tried. Increasing the layers of silica coating printed up to three achieve did increases in transmittance of visible light of 3% or greater.

Hollow silica initially showed greater promise. The void space created due to the hollow spheres creates a smaller refraction index. However with printing, the films were not thick enough (See Figure 4.9). A possible reason to this is that the concentration of suspended particles in the ink is lower than for the solid silica. It is not certain what the reasoning for this is. A possible explanation is due to differences in how the particles are made. The ratio of TEOS to solvent in the hollow silica recipe is about a fourth of the ratio of TEOS to solvent in the solid silica recipe. Another possible explanation comes from the process of developing the ink. Particles are mixed with a binder and then filtered to remove larger particles before being inserted into the ink cartridge. If the particles bind up before filtering, the particles will not make it into the cartridge for printing while the solvents will. Future work can be done to investigate why the hollow silica films do not print as thick of films as the solid silica. Solving this issue will improve the ability to optimize printing of a hollow silica film so that the transmittance may reach suitable levels.

5.3 Mechanical Resistance of Anti-Reflective Films

Both the solid silica films and hollow silica films show promise of obtaining strong mechanical resistance. There is room for improvement for both. For the best solid silica film the increase of light transmittance compared to bare glass appears to only go down slightly after the mechanical resistance test. The relative decrease in performance across the whole visible spectrum however was 33%. This value was calculated using Equation 4. The goal for adequate mechanical resistance is close to 1% decrease across the spectrum. In some cases the film was thicker than the ideal thickness and the mechanical resistance increased the transmittance. While that was good for the transmittance performance of the sample, this result was not good for the mechanical resistance performance.

The hollow silica had some samples with good mechanical resistance but due to the low transmittance very few were tested. The sample shown above did show some promise that the film can obtain adequate mechanical resistance with future work. It is important to not however that to obtain the mechanical resistance the substrates were baked at temperatures of 300 °C. This has a potential conflict for the coating of screens on post market electronics which may not be able to withstand being baked at such high temperatures. An available approach to this issue that was not tested is to cure the film at 60 °C for 1 day or at room temperature for an extended time period.

5.4 Resolution of Anti-Reflective Films

With printed patterns such as the “OSU” pattern the film appears to have sharp resolution to the eye. On a millimeter scale the printer has strong resolution. SEM imaging of the films edges however shows that the printer does not have a high resolution on the micro scale. On the block patterns the ink shows a slight ruffled edge and on the “OSU” pattern a thin single layer of particles was found outside the defined print pattern (Figure 4.14).

5.5 Clogging of Ink Cartridge for Inkjet Printer

A major issue that arose for this project was the clogging of ink cartridges. Not only did this complication hold up progress numerous times but was an issue that had to be solved if this process was to be considered feasible. The printer itself had numerous cleaning methods to combat clogging. While idling, the printer would tickle the nozzles to agitate liquid sitting at the nozzle head. It was also possible by command to have the printer spit or purge. Spitting was act where the printer sent a voltage to each nozzle jet to in rapid succession to shoot at many droplets. For the purge cleaning cycle the printer injected air around a bag that is the ink reservoir. The air creates extra pressure and ejects a stream of ink through the nozzles clearing out particles that may be blocking the nozzle head or microchannels. Appendix 3 provides pictures of the printer (Figure A3.1), ink cartridge and reservoir (Figure A3.2- Figure A3.3), and SEM images of an unclogged nozzle (Figure A3.4) and a clogged nozzle (Figure A3.5).

While printing the cleaning mechanisms programed into the printer worked well as long as the user was attentive and monitored the cartridge and ran the cleaning cycles shortly after the occurrence of a clog. The cleaning cycles are of no use while the printer is not running. Initial method to combat the clogging that occurred was by simply wiping the nozzle head with a KIM wipe that was soaked in isopropyl alcohol. This solution was effective initially until the binder solution was added into the ink. After mixing in the binder solution to the entire process the severity of the clogging issues increased greatly.

The next step added was to produce a cleaning solution. This solution was made up the solvents for the inks and did not contain the NPs of the binder. After printing, the cleaning solution would be attached to the nozzle head and allowed to purge and eject the solution. This helped improve the lifespan of the ink cartridges but clogging was still an issue. To make the struggle worse more binder needed to be added to help further improve the mechanical resistance.

The issue of clogging kept persisting and presenting more challenges. Two strategies played in my experiment were employed to try and alleviate the issue. One strategy was to take clogged cartridges and try to find methods to unclog them. The other strategy attempted to prevent clogging by jerry-rigging the cartridge system so that the particles and binder did not mix until they entered the cartridge. This attempt removed the cartridge reservoir and instead attached a microchannel connected to a micro-mixer. The NPs and the binder were placed into separate syringes and sat on a syringe pump that added slight pressure to the system pushing the solutions into the micro-mixture and into the ink chamber. The printer was able to print with this system in place. However it was a much more complicated system that took a long time to set up and did not obviously help the clogging. While the system was running it worked fine at preventing clogging but the printer often sits idle and the binder and NPs still sat together at this point in time in microchannels clogging it up.

The attempts to unclog cartridges varied. The most effective was to take the cleaning solution and place it in a syringe and spray it through the cartridge. While this alleviated the clogging slightly it did get rid of the problem and introduced extra stress on the nozzle plate. After multiple times of unclogging nozzle heads the heads often broke and stopped working entirely.

Another path taken was to sonicate the clogged cartridges. Sonicating in ethanol helped clean out cartridge heads but ultimately only lengthens the life span of a cartridge as clogging started to occur. This did lead to a future solution however. While the initial attempt was to sonicate clogged cartridges a later attempt was to sonicate the cartridge after every day of printing for 30 minutes. Since this process has been started only one cartridge has clogged up. That cartridge however was sonicated in the same recycled ethanol time after time again. After the cartridge clogged up, the ethanol used to sonicate the cartridge was examined and observed to have notable particulates visible to the eye suspended within it. Any of these particles could have made their way into the channel system connecting the ink reservoir and the nozzles and clog up the entire system. The other two cartridges being used for printing however have maintained the use of all 16 nozzle heads.

6. Conclusion

The objective of the project was to determine the feasibility of printing coating anti reflective thin films of solid and hollow silica NPs as a novel coating technology compared to spin and dip coating. Results have shown that it is firstly possible to print the particles in various patterns and secondly that the performances in transmittance and mechanical resistance of print coated samples can come close to the same performance yielded with conventional methods. Solid silica NPs were coated onto glass samples and improved the light transmittance from about 90% across the visible spectrum to about 93% in champion samples. Hollow silica NPs increased the transmittance to just over 92% of light transmitted in the visible spectrum for champion samples. Suitable mechanical resistance was obtained for the hollow silica NPs in a champion samples but the vast majority were not. Hollow silica NPs in general though showed better mechanical resistance than solid silica. If the transmittance can be improved by obtaining a thicker film than the hollow silica NPs show more promise to be a viable film than the solid silica NPs due to the better mechanical resistance. Work needs to be done with the ink development of the hollow silica to help improve the film thickness per layer of printing. Currently 5 layers of printing hardly coat the glass surface. This likely is due to a low concentration of silica NPs in the ink that ejects out of the nozzle. The largest issue in terms of a feasible process that occurred was the clogging of the ink cartridges. With proper care of the ink cartridges being taken the clogging can be minimized if not completely solved. With future work put in to increase the mechanical resistance and further optimize the transmittance the print coating of silica NPs can be a completely viable deposition process. The process could be used to coat electronic screens, eye glasses and small optical devices. It is also feasible that the process could eventually be scaled up to coat larger objects such as solar panels.

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Appendix 1. SEM Imaging

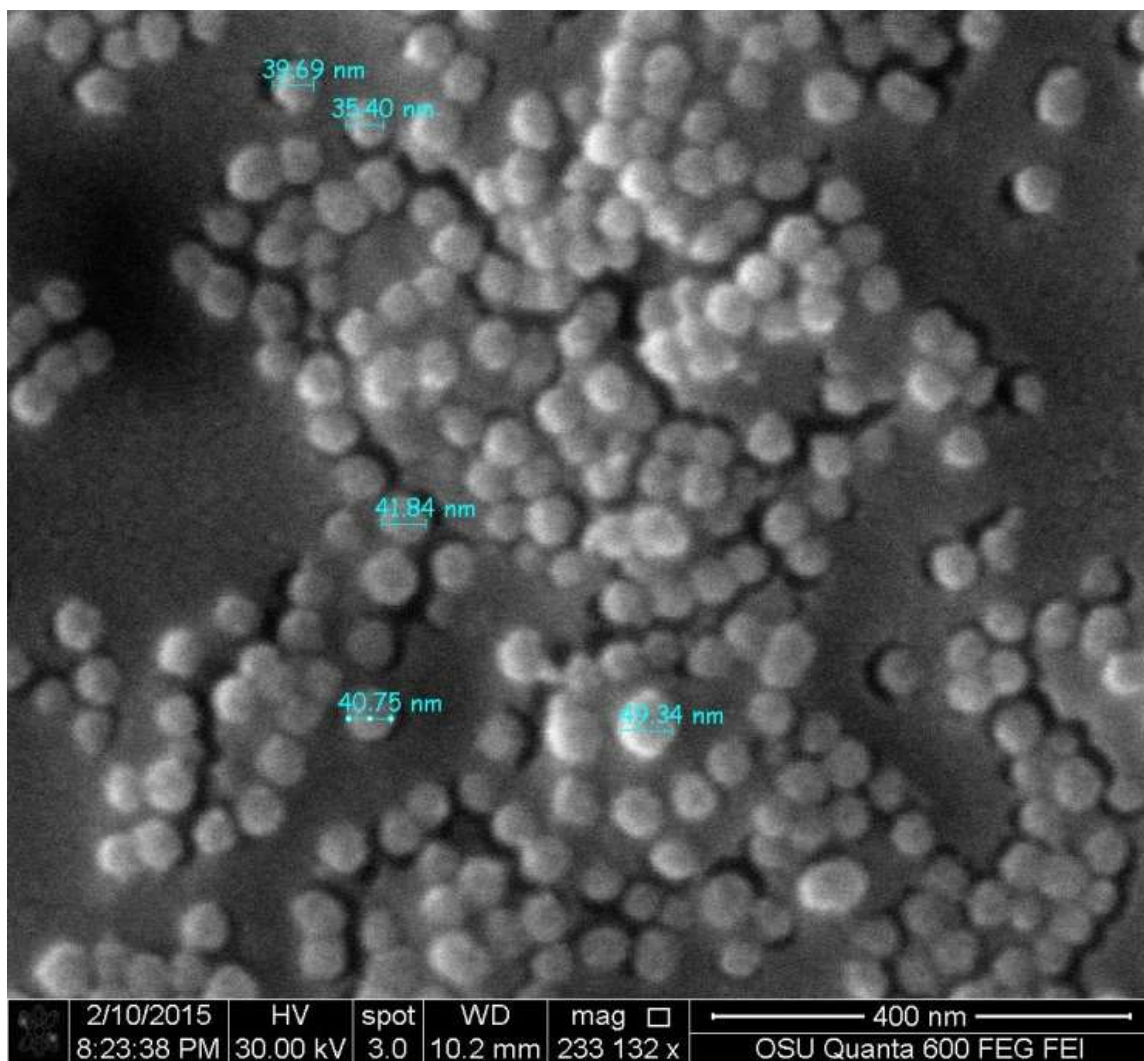


Figure 15: SEM image of hollow silica coating. Image shows diameter measurements of particles to be around 40 nm in diameter

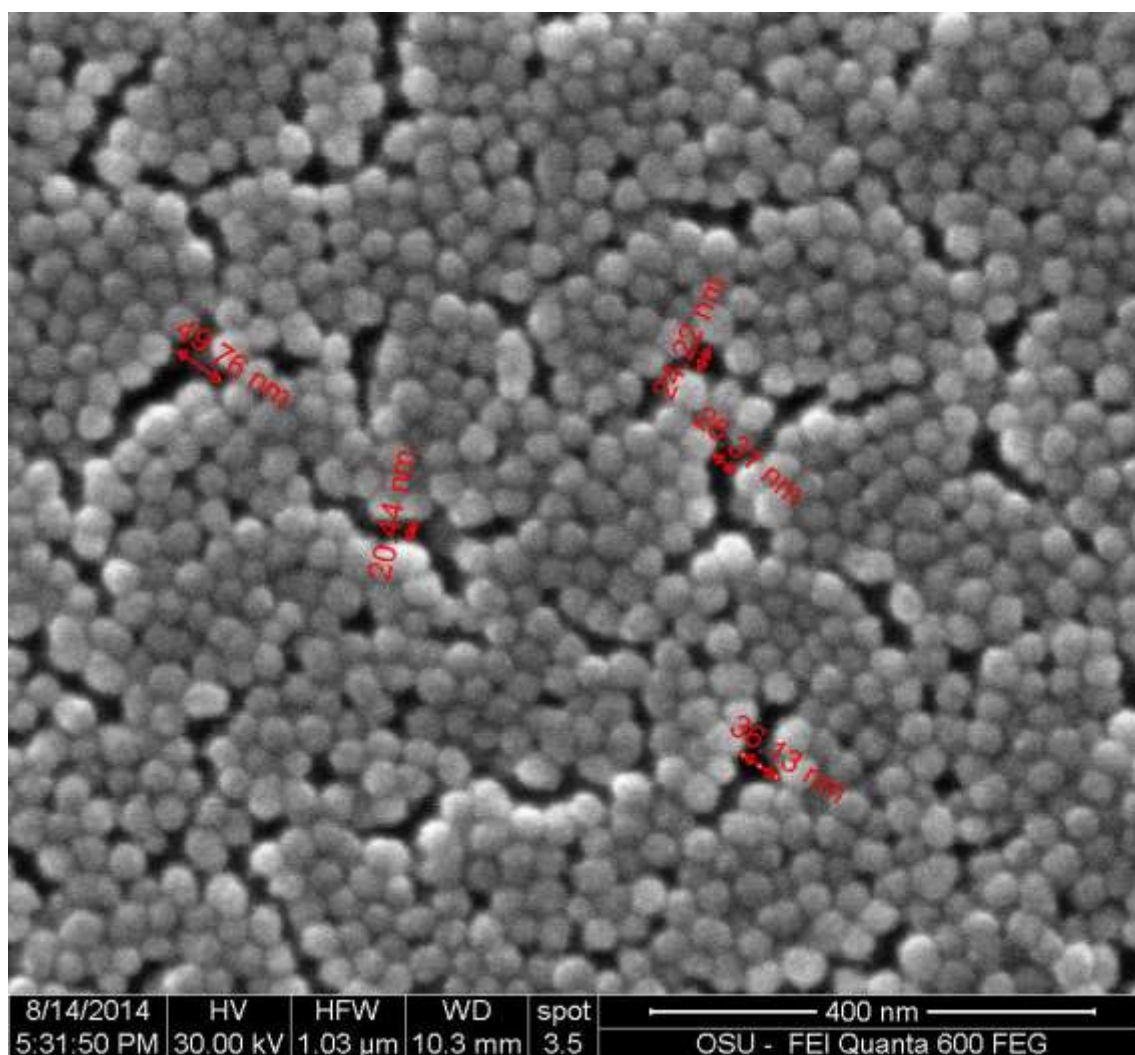


Figure 16: SEM image of Solid Silica particles. Single layer Coating. Gaps in between particles measured out.

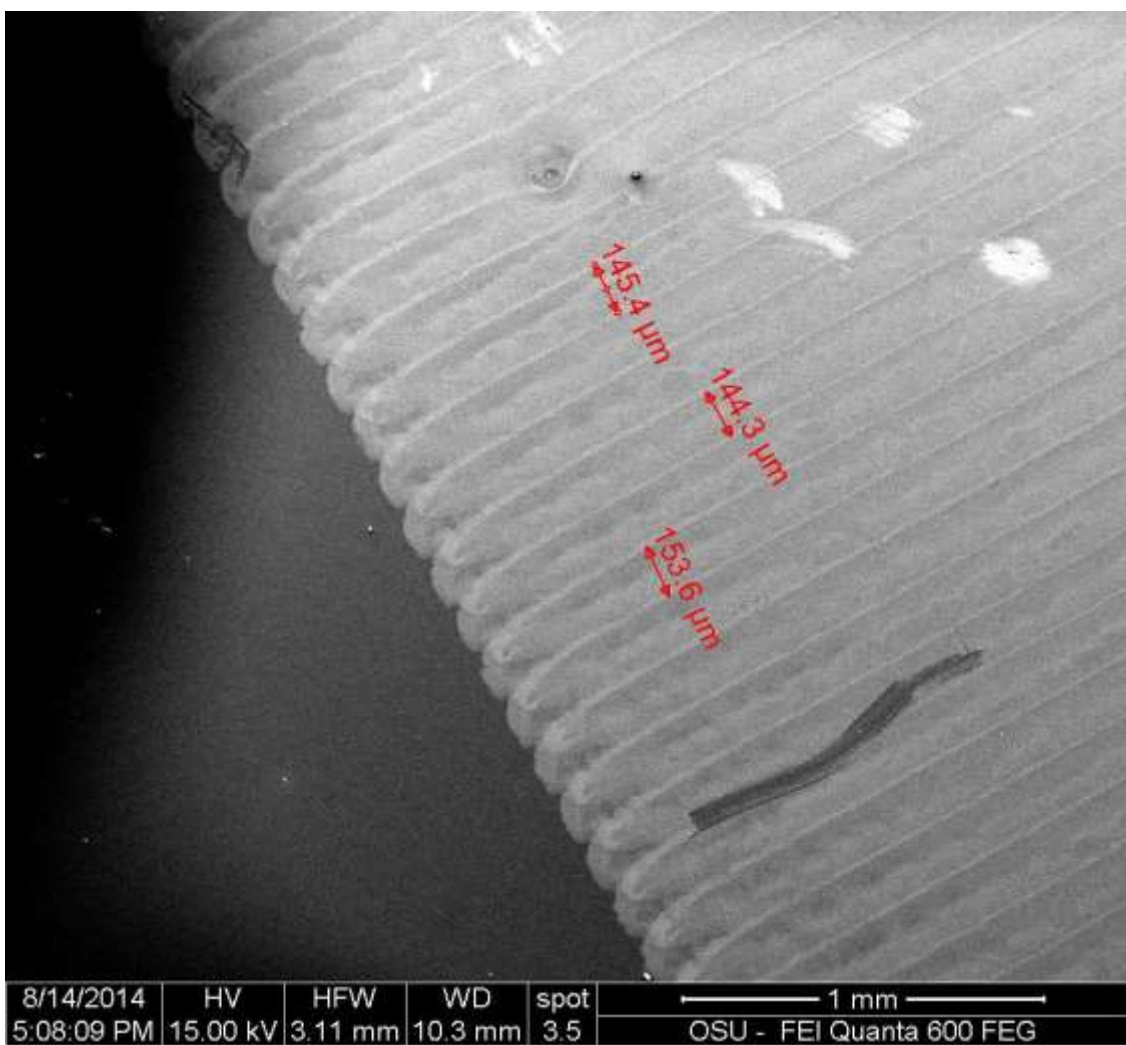


Figure 17: SEM Image of solid silica single layer coating. Measurement of line thickness. Lines are induced by the printing process.

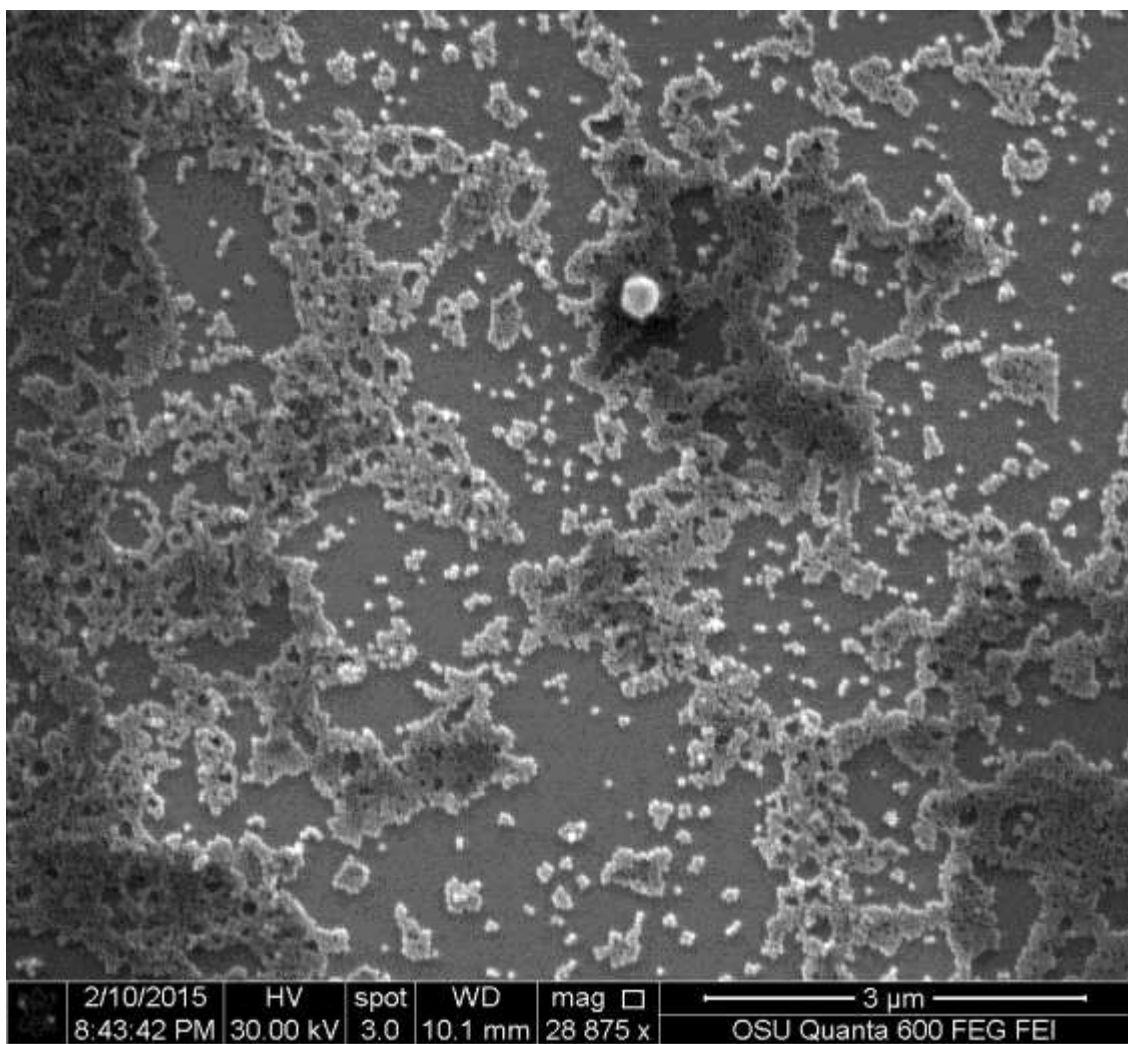


Figure 18: SEM Image of 5 layer coating of hollow silica particles. Coating is incomplete with immense gaps lacking coating despite the five layers of printing.

Appendix 2. Total Light Transmittance Data

A2.1 Solid Silica

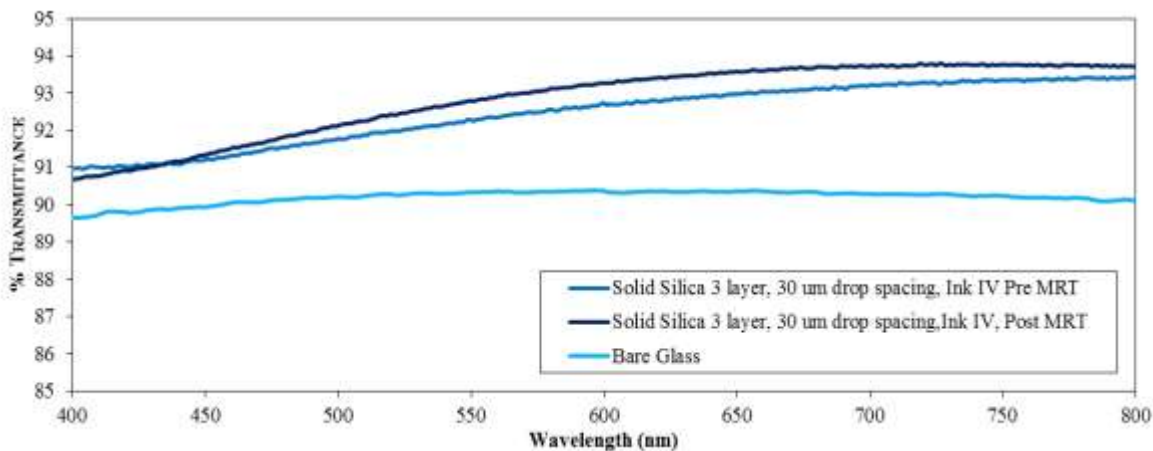


Figure 19: Transmittance and mechanical resistance data for sample print coated with 3 layers of solid silica nanoparticles at 30 μm drop spacing. The transmittance increased after the mechanical resistance. It is suspected that the film was slightly too thick and that the resistance test decreased the film thickness resulting in better transmittance.

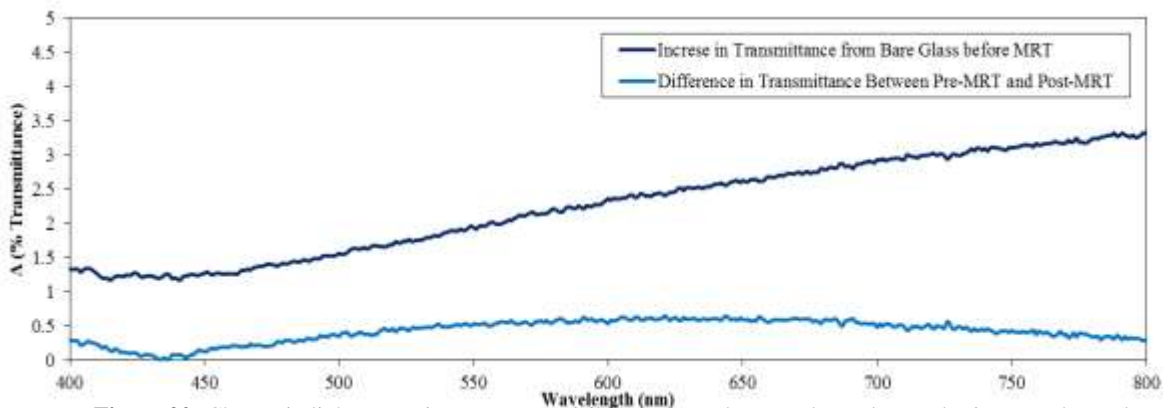


Figure 20: Change in light transmittance across visible spectrum between bare glass and print coated sample, and between the sample before and after the mechanical resistance test.

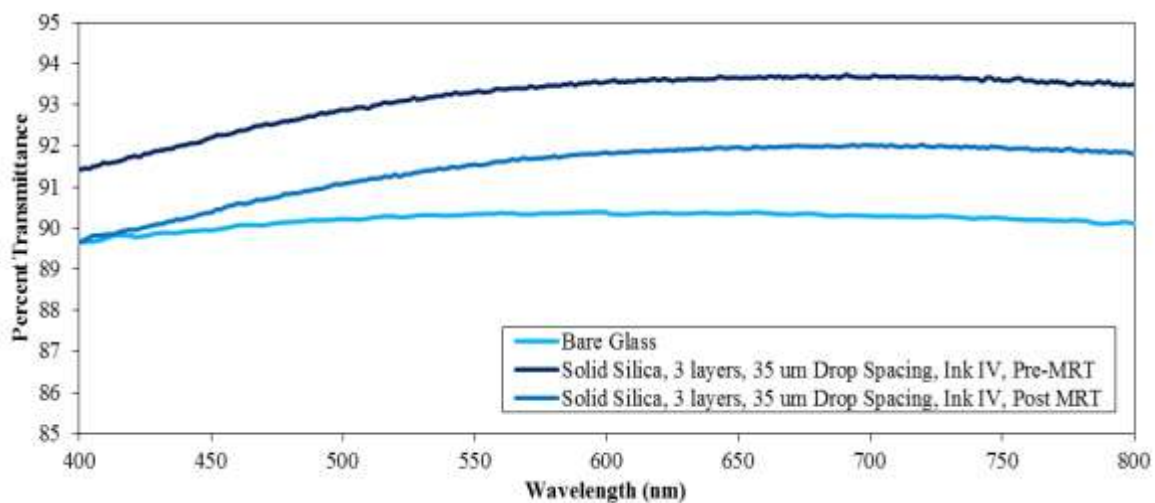


Figure 21: Transmittance and mechanical resistance data for sample print coated with 3 layers of solid silica nanoparticles at 35 μm drop spacing. Initial increase in transmittance was great but mechanical resistance was very low. Sample was printed under same conditions as the sample presented in the results section.

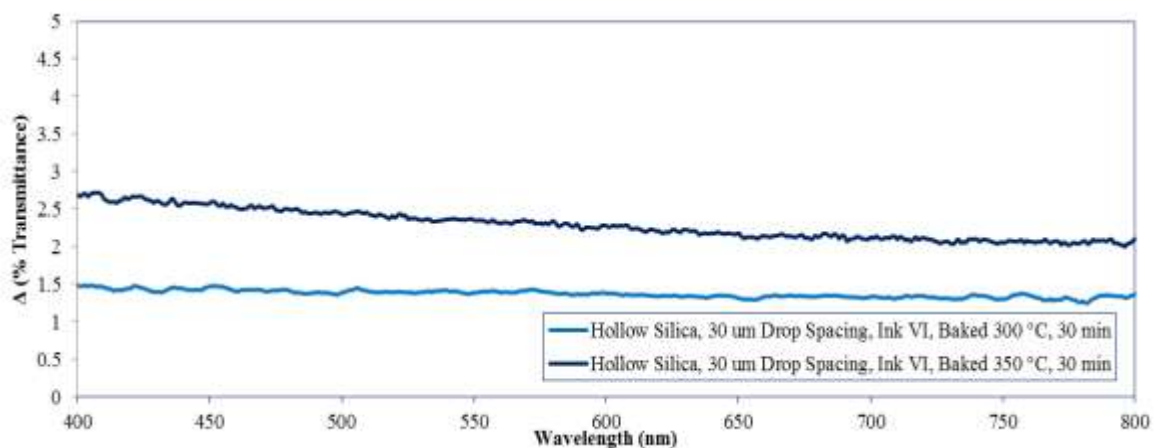


Figure 22: Change in light transmittance across visible spectrum between bare glass and print coated sample, and between the sample before and after the mechanical resistance test.

A2.2 Transmittance and MRT Data for Hollow silica samples

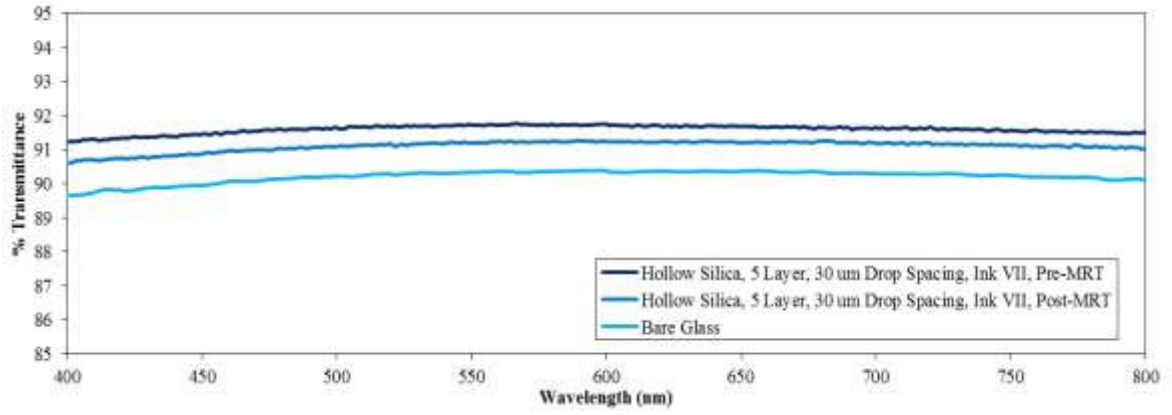


Figure 23: Transmittance data for sample print coated with 5 layers of hollow silica, Ink IV and 30 um drop spacing. Increased transmittance was low and mechanical resistance was not adequate.

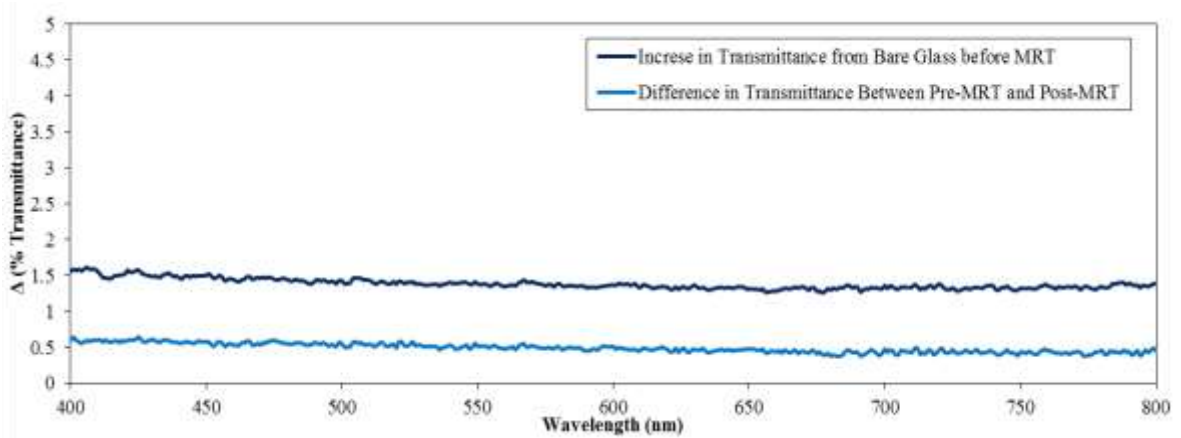


Figure 24: Change in light transmittance across visible spectrum between bare glass and print coated sample, and between the sample before and after the mechanical resistance test.

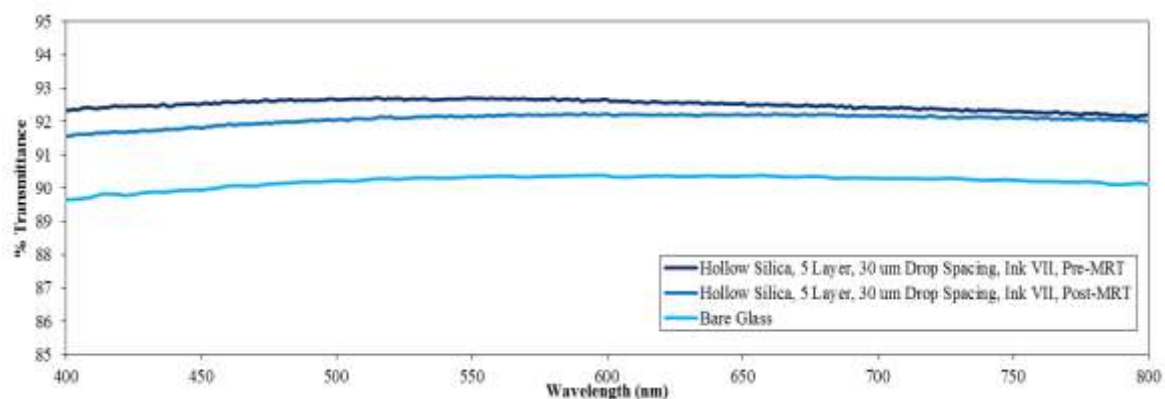


Figure 25: Transmittance data for sample print coated with 5 layers of hollow silica, Ink IV and 30 um drop spacing. This was third replicate that is presented in this paper. The sample had better transmittance than other samples printed with the same conditions but the transmittance is still low relative to the slid silica coatings.

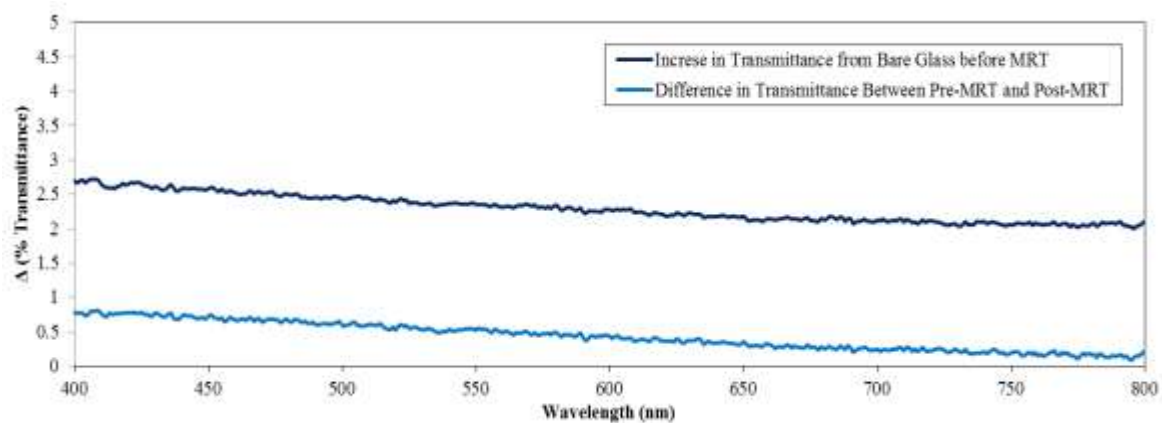


Figure 26: Change in light transmittance across visible spectrum between bare glass and print coated sample, and between the sample before and after the mechanical resistance test.

Appendix 3. Imaging of Inkjet Printer System



Figure 27: Image of the DMP-2831 Printer used for experiment under a hood.

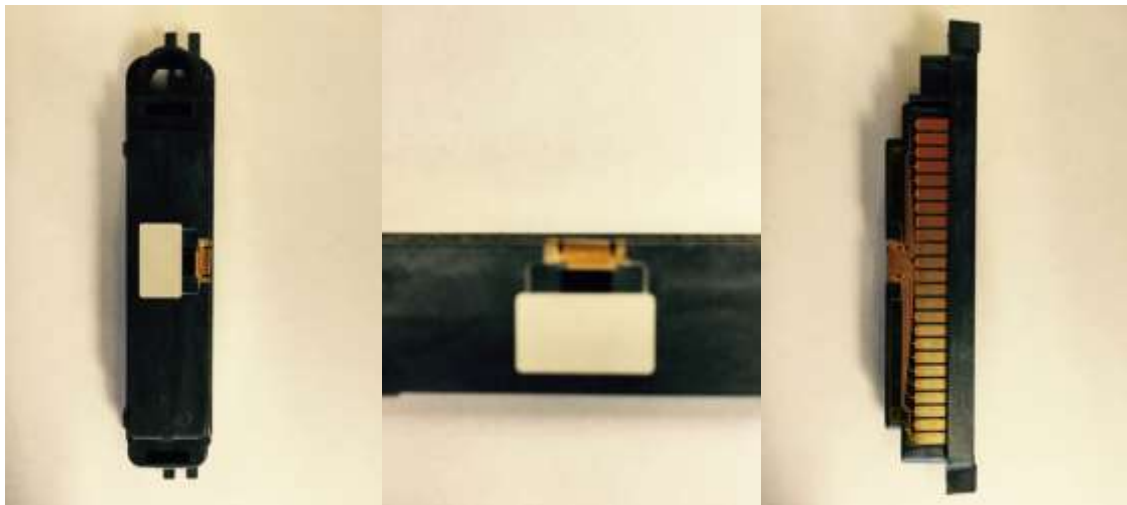


Figure 28: (A) Bottom of ink cartridge nozzle. (B) Zoomed in image of nozzle plate on bottom of ink cartridge. (C) Side of ink cartridge.

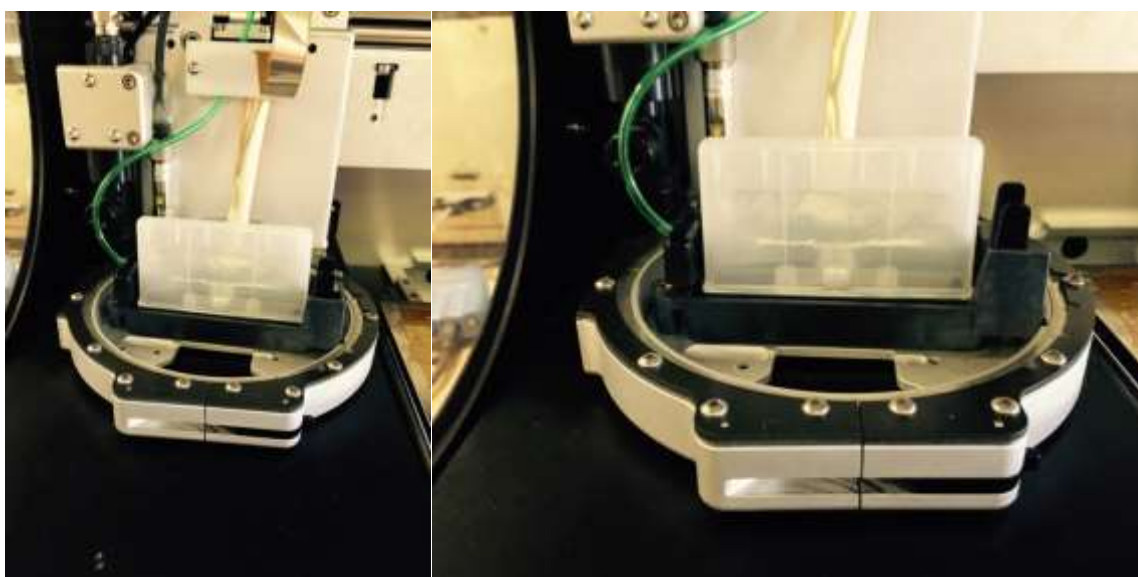


Figure 29: (A) Ink cartridge in reservoir sitting inside printer on cartridge holder. (B) Zoomed in image of cartridge on cartridge holder.

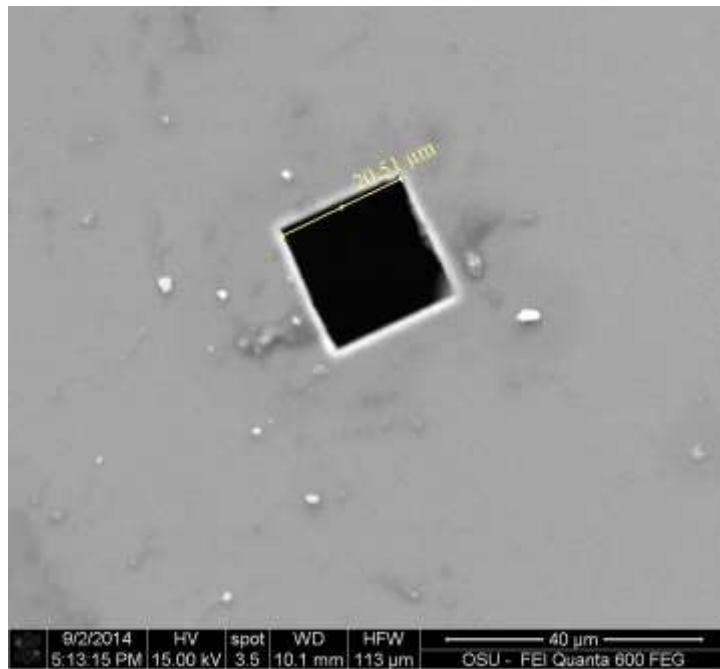


Figure 30: SEM image of ink cartridge nozzle

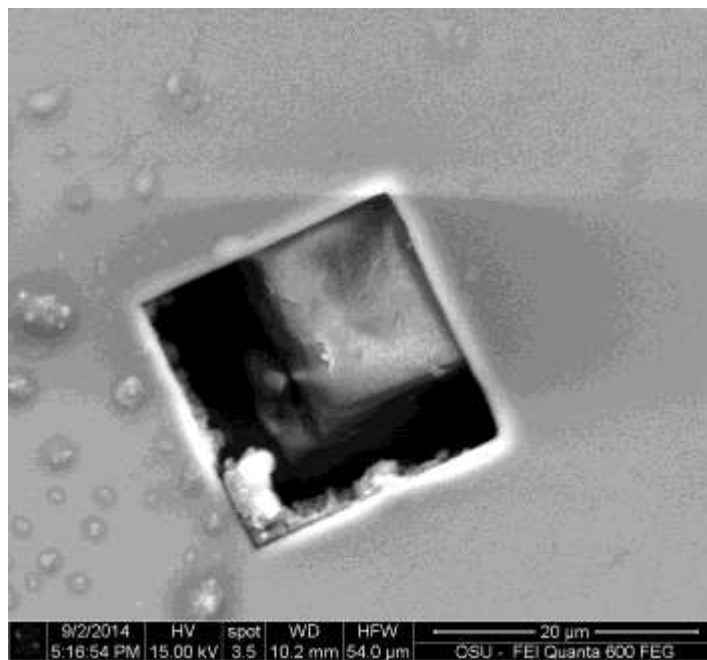


Figure 31: SEM image of clogged cartridge nozzle