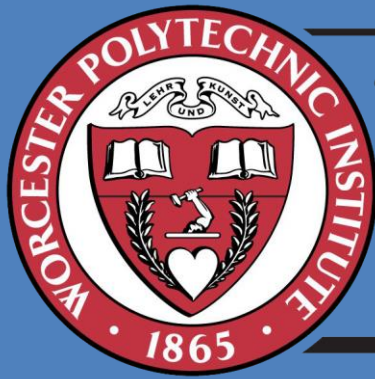




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Silica Aerogels Doped with MWCNT, Graphene, MoS₂, and WS₂

Corey Richards, Evan Baum, Balaji Panchapakesan

Silica aerogels are among the most easily produced types of aerogels due to the availability of required materials, the cheapness of required materials such as carbon dioxide, ethanol, and tetraethyl orthosilicate, and the relatively simple sol-gel chemistry. Using silica aerogels as skeletons, nanomaterials were easily and effectively structured in three dimensions. The aerogels were doped with nanomaterials such as carbon nanotubes, graphene, tungsten disulfide, and molybdenum disulfide by simply dispersing the nanomaterials in ethanol, which acts as the cosolvent during hydrolysis, and mechanically mixing the sol during gelation. The resulting aerogels have properties that are tunable with dopant material and concentration. The doped silica aerogels offer an easy, safe, and affordable alternative to pure carbon aerogels that show catalytic properties.

Introduction

Aerogels are materials that are produced by replacing the pore liquid in a conventional gel with gas. Silica aerogels are of increasing interest recently due to their novel properties and ubiquitous pertinence in a wide variety of technological fields. The silica aerogel has attracted attention specifically for its high porosity, high surface area, low density, low dielectric constant, low thermal conductivity, and high tunability of density [1, 2]. Since the creation of the first silica aerogel in 1931 [3], other materials have been explored for the fabrication of aerogels, including carbon (carbon nanotubes, graphene, and organic materials) and metal oxides [4]. Aerogels have been used as insulators [5], absorbers for chemical spills [6], catalyst carriers [7], Cherenkov radiators [2], supercapacitors [8], and for drug delivery [9].

Silica gels are formed by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) in ethanol [10]. Hydrolysis can be either acid-catalyzed or base-catalyzed. Base-catalyzed hydrolysis of TEOS or TMOS is accomplished through a substitution nucleophilic (bi-molecular) (S_N2) reaction, in which water acts as the nucleophile [11]:

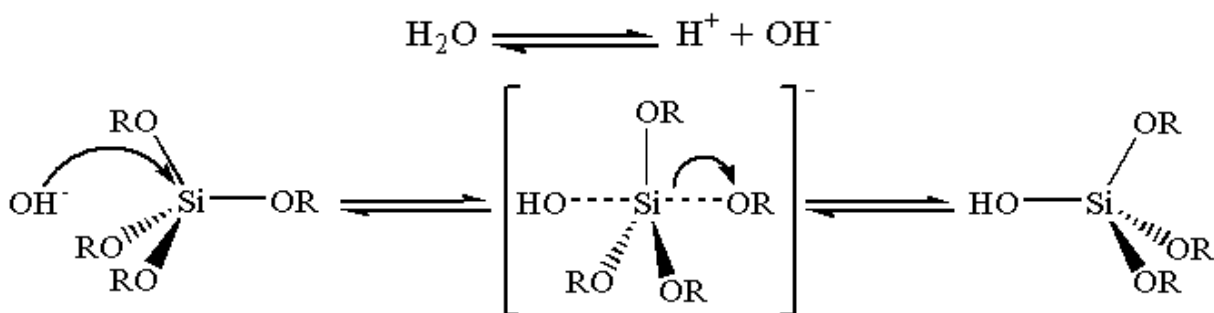


Figure 1: Substitution nucleophilic (bi-molecular) attack on TEOS or TMOS by hydroxide during base-catalyzed hydrolysis. In this reaction, R is a methyl group for TMOS and an ethyl group for TEOS.

During acid-catalyzed hydrolysis, an alkoxy group is rapidly protonated, resulting in a withdrawal of electron density from the silicon atom, making it more electrophilic. The silicon atom is then attacked by water in an S_N2 -like fashion [11]:

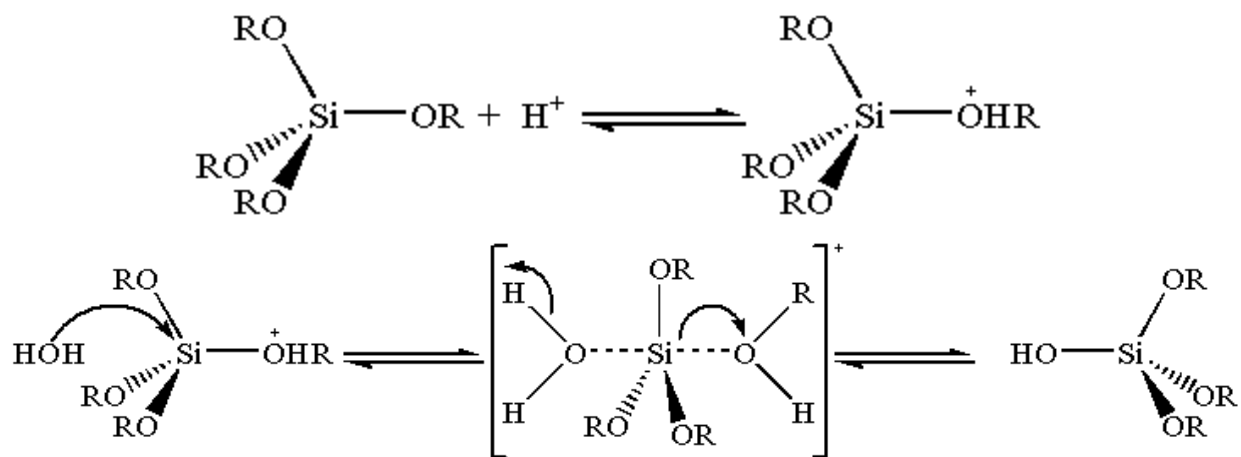


Figure 2: Substitution nucleophilic (bi-molecular)-like attack on protonated TEOS or TMOS by water during acid-catalyzed hydrolysis. In this reaction, R is a methyl group for TMOS and an ethyl group for TEOS.

Multiple alkoxy groups may be substituted with OH during hydrolysis.

Polymerization occurs via the formation of siloxane bonds during the condensation reaction [10]. For base-catalyzed condensation:

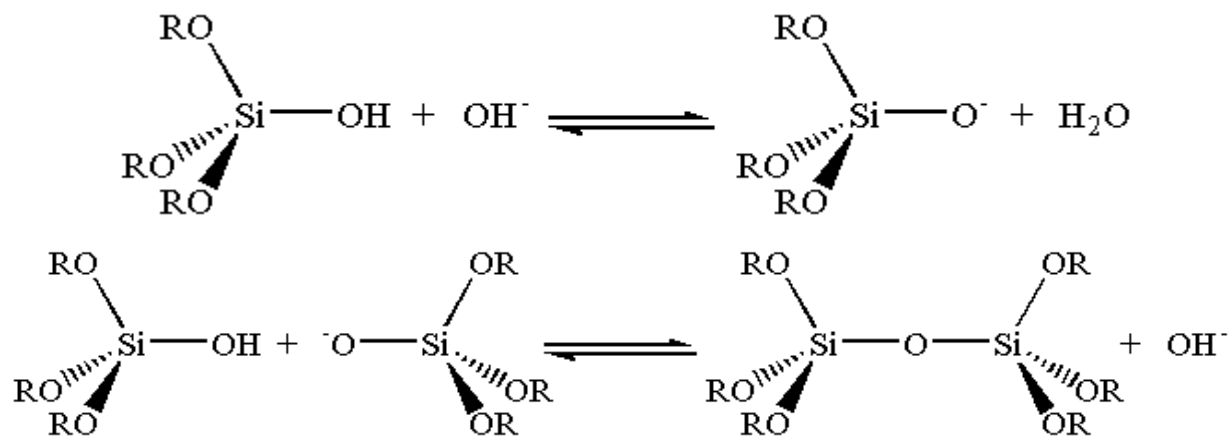


Figure 3: Polymerization mechanism for base-catalyzed condensation reaction. Free radical polymerization occurs during base-catalyzed condensation [10].

And for acid-catalyzed condensation:

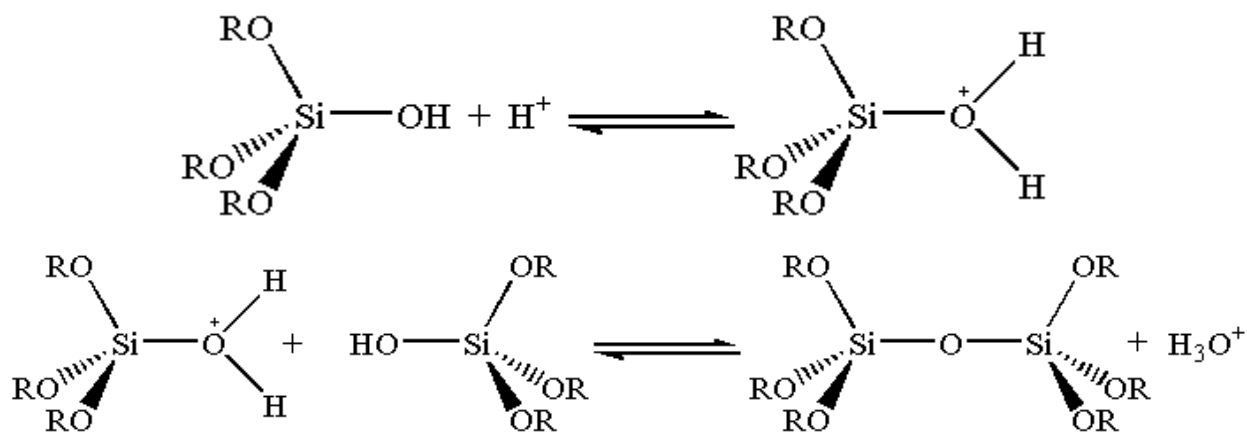


Figure 4: Polymerization mechanism for acid-catalyzed condensation reaction. Cationic polymerization occurs during base-catalyzed condensation [10].

In acid-catalyzed gelation of TMOS or TEOS, the condensation reaction is slow and limits the speed of the gelation, while in base-catalyzed gelation hydrolysis is the limiting step [11].

A process called supercritical drying can be used to produce a silica aerogel by replacing a gel's pore liquid with gas. During supercritical drying, the temperature and pressure of a gel's pore liquid is raised above its critical point, where it becomes a supercritical fluid. When a supercritical fluid is depressurized, its density decreases continuously, preventing shrinkage of the gel's pores via capillary action. If a pore liquid is evaporated below its critical point, a sharp decrease in density occurs as the liquid is vaporized, causing the gel's pores to shrink due to the capillary forces [12].

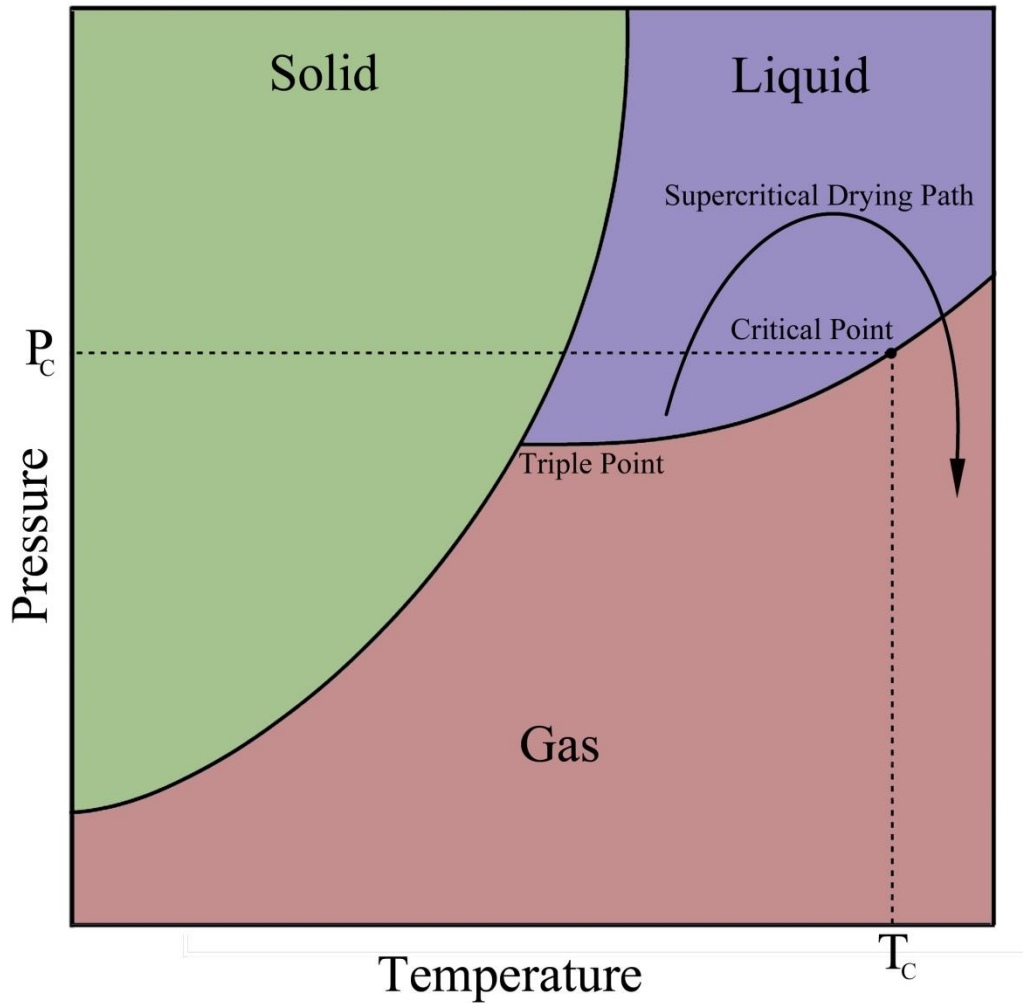


Figure 5: Pressure-temperature pathway for supercritical drying. To avoid rapid vaporization and hence pore shrinkage, the pressure and temperature are increased above the pore liquid's critical point. A fluid that is above its critical point experiences a continuous change in density when depressurized, preventing gel shrinkage. For carbon dioxide, the critical pressure is 1,071 psi and the critical temperature is 31.1°C.

Supercritical drying can be a hazardous process if the pore liquid's critical temperature and pressure are high. For this reason, a gel's pore liquid is often exchanged for another liquid which has a lower critical temperature and pressure. Often, the liquid entrapped within a gel's network is exchanged for liquid carbon dioxide (CO_2). Since CO_2 has a critical temperature of 31.1°C and a critical pressure of 1,071 psi, it can safely be supercritically dried at slightly above ambient temperature [12].

Carbon was being explored as a main aerogel component as early as the late 1980s by researchers such as R. W. Pekala and F. M. Kong [13, 14]. These organic aerogels were made by first mixing formaldehyde and resorcinol and catalyzing the polymerization with sodium

carbonate. The forming gels were then cured at near 100°C for up to seven days and placed under dilute acid and then supercritically dried. Finally, pure aerogels were produced by pyrolyzation at 1100°C [13, 14]. Carbon aerogels made headlines in 2010 when Zou et al. fabricated an ultralow density multiwalled carbon nanotube aerogel (MWCNT) [15]. This was accomplished by mixing poly(3-(trimethoxysilyl) propyl methacrylate) with MWCNT in chloroform solution. The poly(3-(trimethoxysilyl) propyl methacrylate) helped to form bonds between the MWCNTs during hydrolysis and condensation. Freeze drying was used to fabricate the final aerogel instead of supercritical drying [15]. The benefits of carbon aerogels are their highly controllable densities, high porosities, low thermal conductivities, and relatively high electrical conductivities, making them favorable materials for electronics [15-17].

For this paper, silica aerogels were doped with various materials including MWCNT, graphene, tungsten disulfide (WS_2), and molybdenum disulfide (MoS_2). Using silica networks as skeletons offers a cheap and easy way to structure nanomaterials in three dimensions. The properties of these aerogels cannot compete with other aerogels such as carbon aerogels in many areas, but are cheaper, safer, and easier to fabricate, and still offer controllable porosity, density, conductivity, thermal conductivity, and absorbance. For instance, high temperature furnaces and acids are not required to make the doped silica aerogels.

Materials

TEOS was used over TMOS as the source of silica because TMOS is highly reactive and can cause deposition of silica in human lungs and eyes much more easily than TEOS can [18]. TEOS was purchased from Sigma Aldrich® at $\geq 99.0\%$. Base-catalyzed gelation was used because of the fast condensation reaction associated with using a base-catalyst and because acid-catalyzed gels can undergo significant shrinkage during supercritical drying [12]. An ammonium fluoride/ammonium hydroxide stock solution was prepared as the catalyst solution. 200-proof ethanol was used as a co-solvent. Ethanol is miscible with both TEOS and water, which are immiscible under normal circumstances, allowing them to react with each other. Ethanol also results in a small change in gel volume when solvent exchanged with liquid carbon dioxide. Various materials were purchased to be used as dopants for the aerogels. 8 nanometer diameter MWCNT with $>95\%$ purity was purchased from Cheap Tubes®, single layer graphene powder was purchased from ACS Material®, and ultrafine MoS₂ and WS₂ powder was purchased from Graphene Supermarket®. A Samdri®-PVT-3D critical point dryer was purchased from tousimis®. Bone dry liquid CO₂ was purchased from Airgas®.

Results

The ammonium fluoride/ammonium hydroxide stock solution was prepared by adding 1.85 g of ammonium fluoride and then 22.8 mL of ammonium hydroxide to 100 mL of water. To form a silica aerogel, two separate solutions were prepared in separate vials, the alkoxide solution and the catalyst solution. The alkoxide solution was prepared by mixing 0.145 mL TEOS with 0.32 mL ethanol. The catalyst solution was prepared by mixing 0.205 mL water, 0.32 mL ethanol, and a drop of ammonium fluoride/ammonium hydroxide stock solution. The catalyst solution was then poured into the alkoxide solution and the mixture was stirred. Gelation occurred within 15 minutes of mixing.

Hybrid silica aerogels were made with the same recipe and procedure as the conventional silica aerogels. However, for the hybrid aerogels, instead of using pure ethanol, ethanol with MWCNT, graphene, MoS₂, or WS₂ dispersed in it was used. About 0.016 g of MWCNT, graphene, MoS₂, and WS₂ were added to separate 20 mL vials of ethanol. The solutions were sonicated for 60 hours before being used. The current over time at a constant one volt was measured for MWCNT-doped sol during gelation using a two-probe setup.

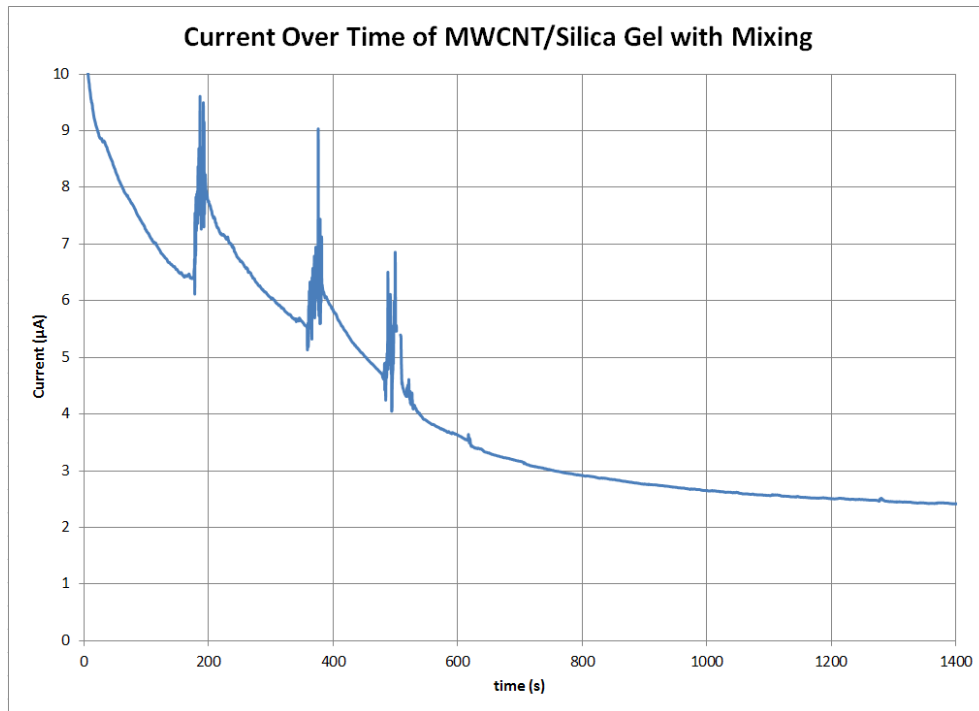


Figure 6: Measurement of current in forming MWCNT doped silica gel over time at a constant voltage. The spikes in current correspond to periods of stirring, suggesting stirring increases uniformity and hence conductivity.

There appears to be some discharging as the current is measured overtime, as seen in Figure 6. The sharp increases in current correspond to brief time periods of stirring the gel. Figure 6 suggests that the most uniform and electrically conductive gels are formed with constant mixing. For this reason the proceeding sols are mixed constantly until there is a sharp increase in viscosity. Once the viscosity increases significantly, the stirring is stopped and the gels are allowed to form without further disturbance.

Silica sols doped with 0.5 mg/mL MWCNT, graphene, MoS₂, and WS₂ were prepared and stirred until a sharp increase in viscosity was observed. During the onset of gelation, probes were inserted into the sols and used to measure the conductivity of the resulting gels. An additional gel with both 0.5 mg/mL MWCNT and 0.5 mg/mL graphene was also formed and its electrical conductivity measured. Once the viscosity increased, the probes of a semiconductor parameter analyzer were placed in the forming gels and the gels were allowed to form around the probes. Current was measured against voltage for each hybrid gel. An un-doped silica gel was also formed to be used as a control.



Figure 7: Visual of two-probed electrical conductivity measurement of forming MWCNT-doped gel.

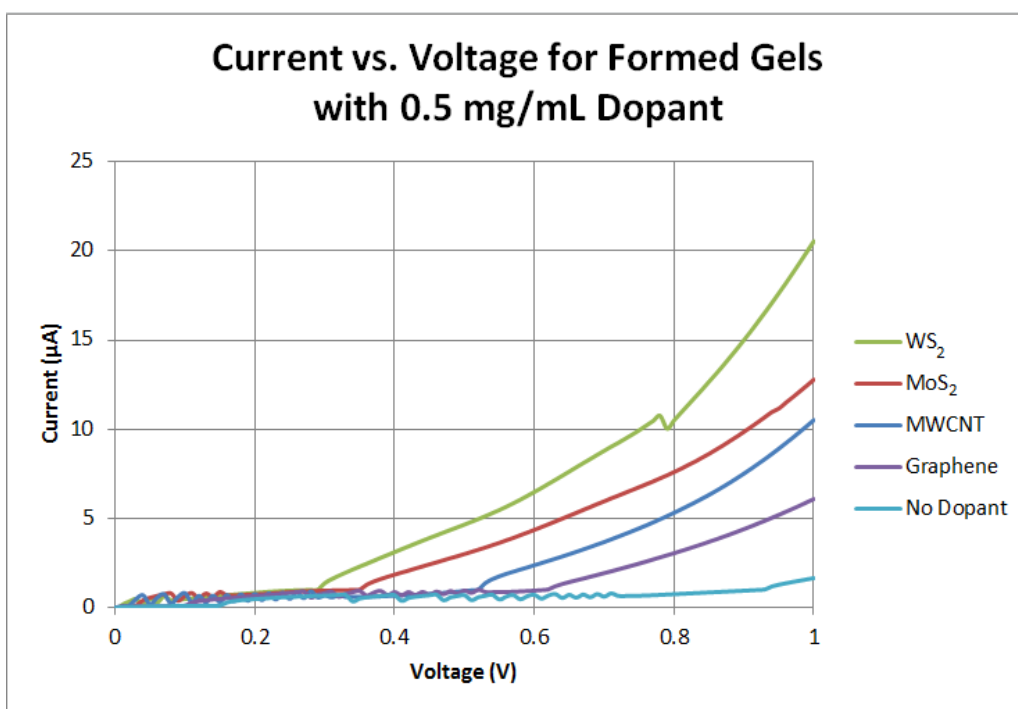


Figure 8: Current vs. voltage for fully stirred gels with various dopants of concentration 0.5 mg/mL.

After the initial conductivity measurements of gels with dopant concentrations of 0.5 mg/mL, the concentration of each dopant was varied. To accomplish this, some of the

ethanol/dopant mixture was replaced with pure ethanol. The conductivities of the gels show a dependence on dopant concentration. The forming gels were stirred as identically as could be accomplished without machine assistance. During some of the measurements for each concentration, the current observed was either higher or lower than the values reported. The typical values observed for each concentration was graphed, however, in the future equipment such as a viscometer should be utilized to stir all the gels identically since stirring rate and time affect gel uniformity and electrical conductivity as demonstrated in Figure 6.

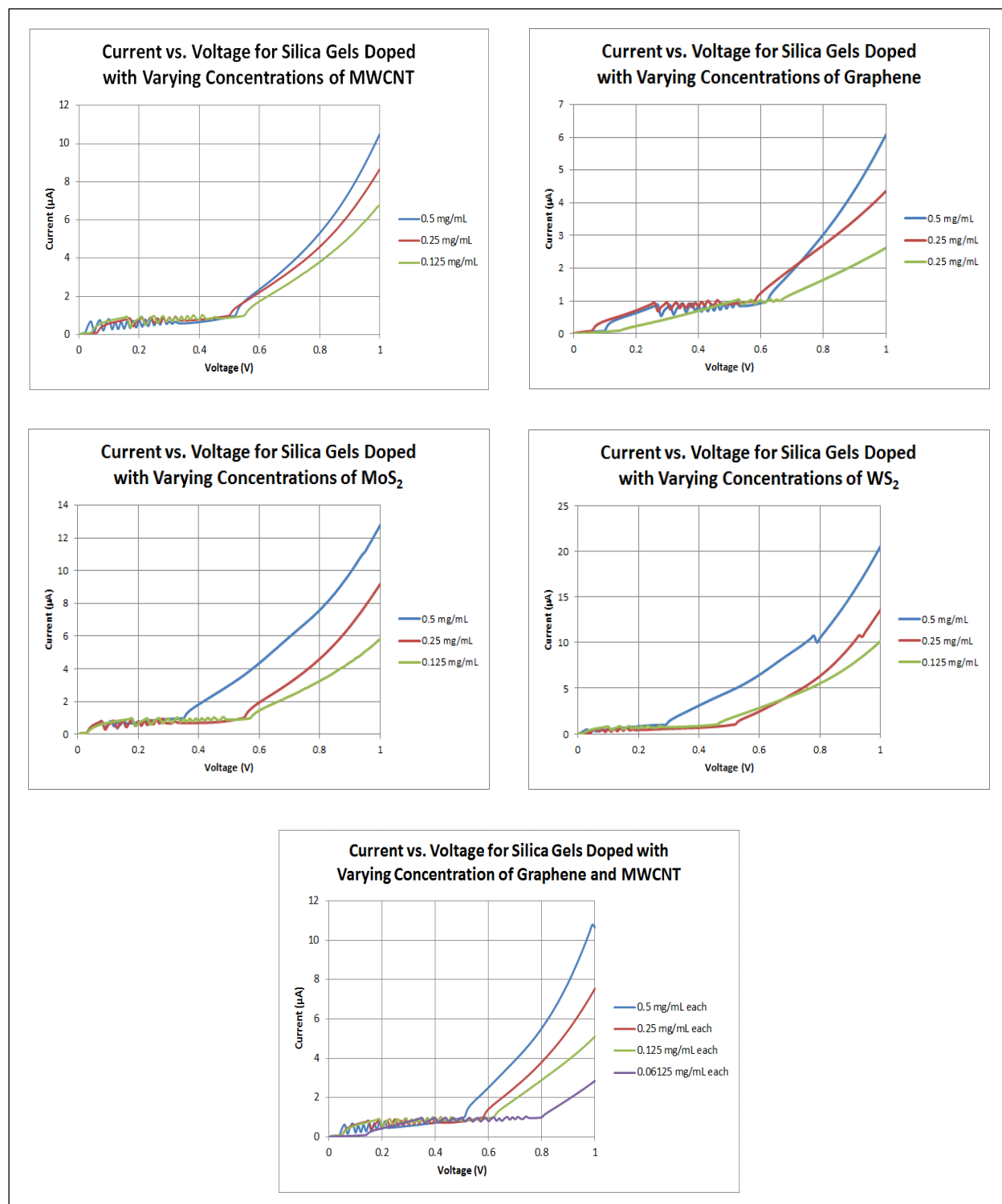


Figure 9: The current was measured against voltage for different concentrations of well mixed sols with MWCNT, graphene, MoS₂, and WS₂ doping during gelation. A correlation between concentration and conductivity was observed, however, many more measurements must be performed to verify these results.

For the fabrication of aerogels, 1 mL sols doped with 0.5 mg of either MWCNT, graphene, MoS₂, or WS₂ were prepared. Syringes with their tops cut off were used as molds. Each sol was poured into a separate mold and stirred until a sharp increase in viscosity was observed. After the onset of the viscosity increase, the forming gels were left undisturbed until the gels formed. Gel formation took between 10 and 15 minutes. The molds were then filled to the top with ethanol, and the gels were allowed to age under ethanol for 24 hours. An additional gel of 1 mL volume doped with both 0.5 mg MWCNT and 0.5 mg graphene was also formed.

After 24 hours, each gel was ejected from the syringe into a separate ethanol bath. In the ethanol bath the water used for hydration that is still entrapped in the gel network diffuses out of the gel; an exchange between ethanol and water occurs. Diffusion occurs since ethanol and water are miscible with each other. Every 24 hours, the gels were transferred into new ethanol baths. Four or five exchanges were performed to ensure all the water had been removed from the gels. Before supercritical drying, the pore liquid must once again be solvent exchanged for liquid carbon dioxide. During this second solvent exchange, the gel often shrinks slightly because the favorable interaction between the pore liquid and the liquid carbon dioxide result in a mixture with molecules that are closer together than in either individual liquid. Different pore liquids cause different amounts of gel shrinkage during the second solvent exchange. Ethanol only results in about a five percent decrease in volume when exchanged with liquid carbon dioxide. For this reason it is important to make sure that all the water entrapped in the gel networks is exchanged with pure ethanol before supercritical drying.

After the solvent exchange between the water and ethanol, the gels were processed in the Tousimis ® supercritical dryer. One gel was processed at a time, while the other gels were stored under pure ethanol. Before supercritical drying, each gel was weighed and then transferred into the supercritical dryer chamber. The following procedure was used for the supercritical drying:

1. Once the gel is transferred into the supercritical drier chamber, pour pure ethanol into the supercritical dryer until the gel is completely submerged.

The ethanol will protect the gel while the chamber is being filled with liquid CO₂ and prevent the ethanol in the gel from evaporating.

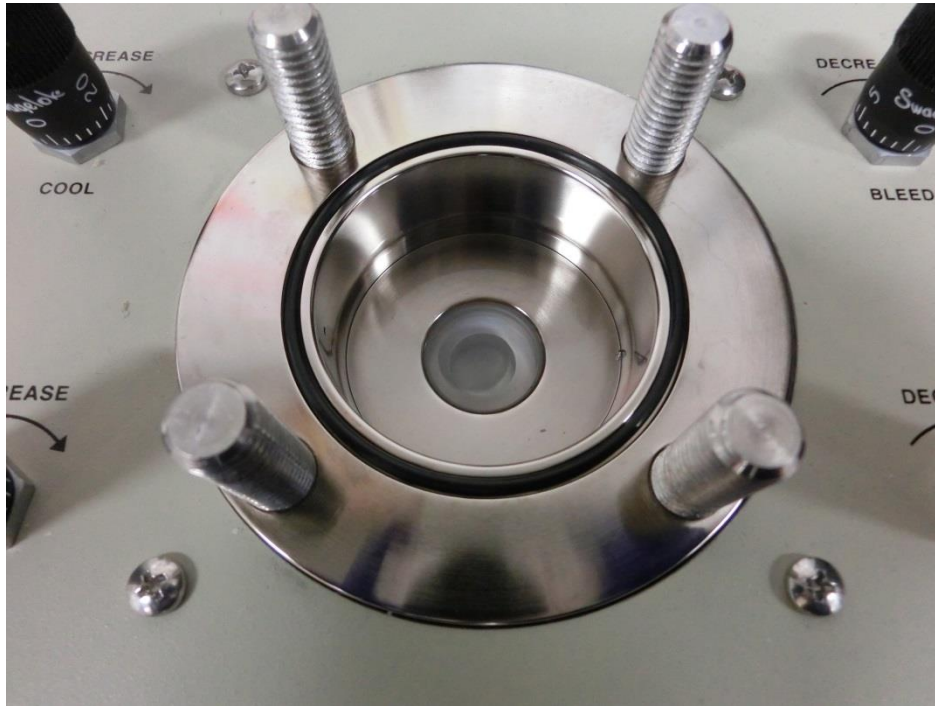


Figure 10: Visual showing the supercritical drying chamber with a gel submerged in ethanol inside and the O-ring secured on the gland.

2. Install the O-ring on the gland and secure the chamber lid, hand-tightening the lug nuts in a star pattern.
3. Turn on the power switches for the processing chamber and the condenser.



Figure 11: Visual showing the chamber lid secured, lug nuts hand-tightened, and processing chamber power turned on (left) and condenser power turned on (right).

4. Open the carbon dioxide tank's valve and the condenser drain valve.



Figure 12: Visual showing the condenser drain valve in the closed position (left) and the open position (right).

5. Open the cool valve to about the “10” position.

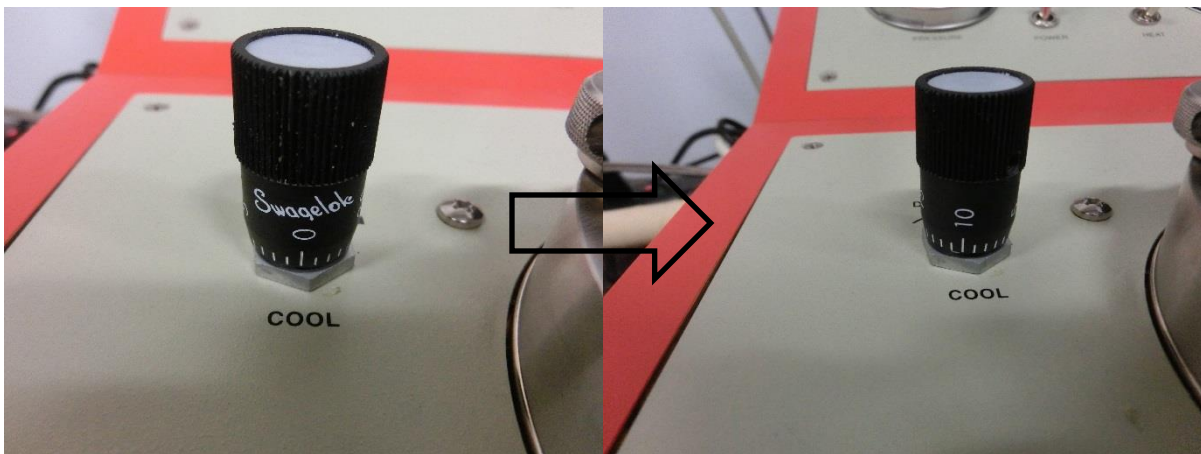


Figure 13: Visual showing the cool valve being opened to the 10 position from the 0 position.

6. Close the cool valve once the chamber is cooled to a temperature between 10°C and 15°C.
7. Open the fill valve to about the “8” position to begin filling the chamber with liquid CO₂. A meniscus will travel across the chamber viewing port when the chamber is full. Leave the fill valve open after the chamber is filled with liquid CO₂.

The pressure difference between the carbon dioxide tank and the supercritical dryer's chamber will cause the liquid carbon dioxide to flow into the chamber. Lowering the

temperature of the chamber ensures that the chamber pressure remain below that of the CO₂ tank.

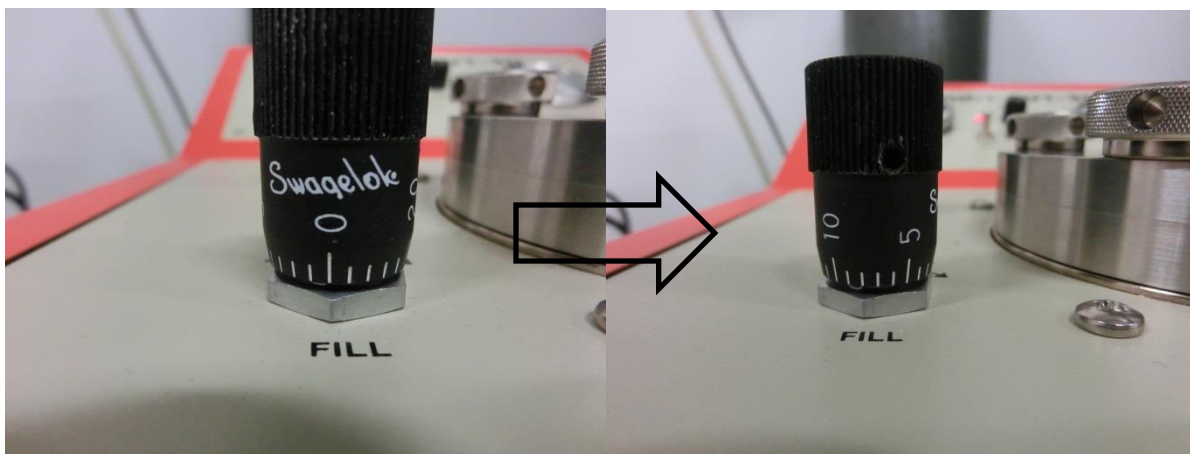


Figure 14: Visual showing the fill valve being opened to the 8 position from the 0 position.

8. Open the purge valve to about the 10 position and purge the chamber for two and a half minutes, ensuring that the gel is always completely submerged in liquid CO₂. Ethanol will be seen flowing out of the condenser drain valve.



Figure 15: Visual showing ethanol flowing out of the condenser drain valve.

9. Open the cool valve again to cool the processing chamber to a temperature between 10°C and 15°C. Close the cool valve once this temperature is reached. Disregard this step if the temperature is already in this range.

10. Allow the chamber to fill with liquid CO₂ again.

After the chamber fills and returns to room temperature the pressure should read about 900 psi.

11. Turn off the processing chamber power switch.

It is very important that the power switch is turned off after step 10. If the power switch is left on, then the chamber temperature can increase to near the critical temperature of CO₂, causing the CO₂ to vaporize and the gel to shrink.

12. Allow solvent exchange to occur between the ethanol and CO₂ for one hour.

Ethanol is exchanged from the gel's pores for CO₂ because CO₂ has a low critical temperature and pressure.

13. Repeat steps 3-12 until no more ethanol can be seen draining from the condenser drain valve during purging.

14. Cool and fill the chamber one last time.

15. Close all chamber valves and the gas tank valve.

16. Turn the processing chamber heat switch on and allow the temperature and pressure to increase. Above 31.1°C and 1071 psi, the CO₂ will be a supercritical fluid.

The pressure will increase to 1400 psi and the temperature will increase to 44°C. The chamber will automatically vent above 1400 psi. Do not turn off the heat switch, the system will automatically maintain itself above the critical pressure and temperature of CO₂.

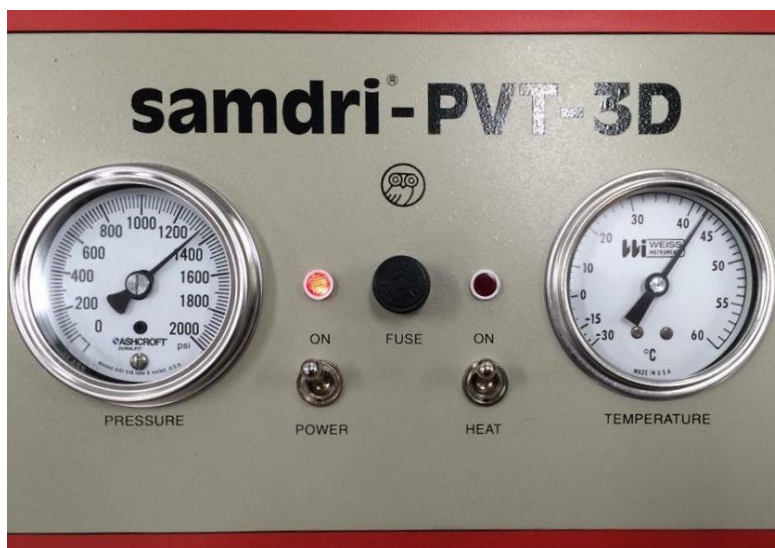


Figure 16: Visual showing the supercritical dryer in heat mode, with a temperature and pressure above the critical point of CO₂.

17. Allow the CO₂ to exist as a supercritical fluid for 20 minutes. After 20 minutes, open the bleed valve to about the “8” position and allow the pressure to slowly drain to 200 psi.
18. Close the bleed valve and open the purge valve slightly. Allow the pressure to completely drain.
19. Open the chamber, remove the aerogel, and weigh it.

Some aerogels were also prepared with less dopant concentration, specifically 1 cubic centimeter samples doped with 0.15 mg of MWCNT and MoS₂ were prepared. The transmittance and absorbance were measured for each fabricated aerogel. A decrease in transmittance and an increase in absorbance was observed in the more heavily doped aerogels, suggesting that doped aerogels can be used for effective light-trapping. Virtually no light is transmitted through the aerogels that are heavily doped with graphene, MWCNT, and graphene plus MWCNT. The transmittance of the aerogels that are more heavily doped with MoS₂ and WS₂ is slightly higher than the carbon-doped aerogels, while transmission of the aerogels lightly doped with MoS₂ and WS₂ is about half that of the un-doped aerogel. These results suggest that the absorbance of these aerogels is highly tunable with dopant concentration.

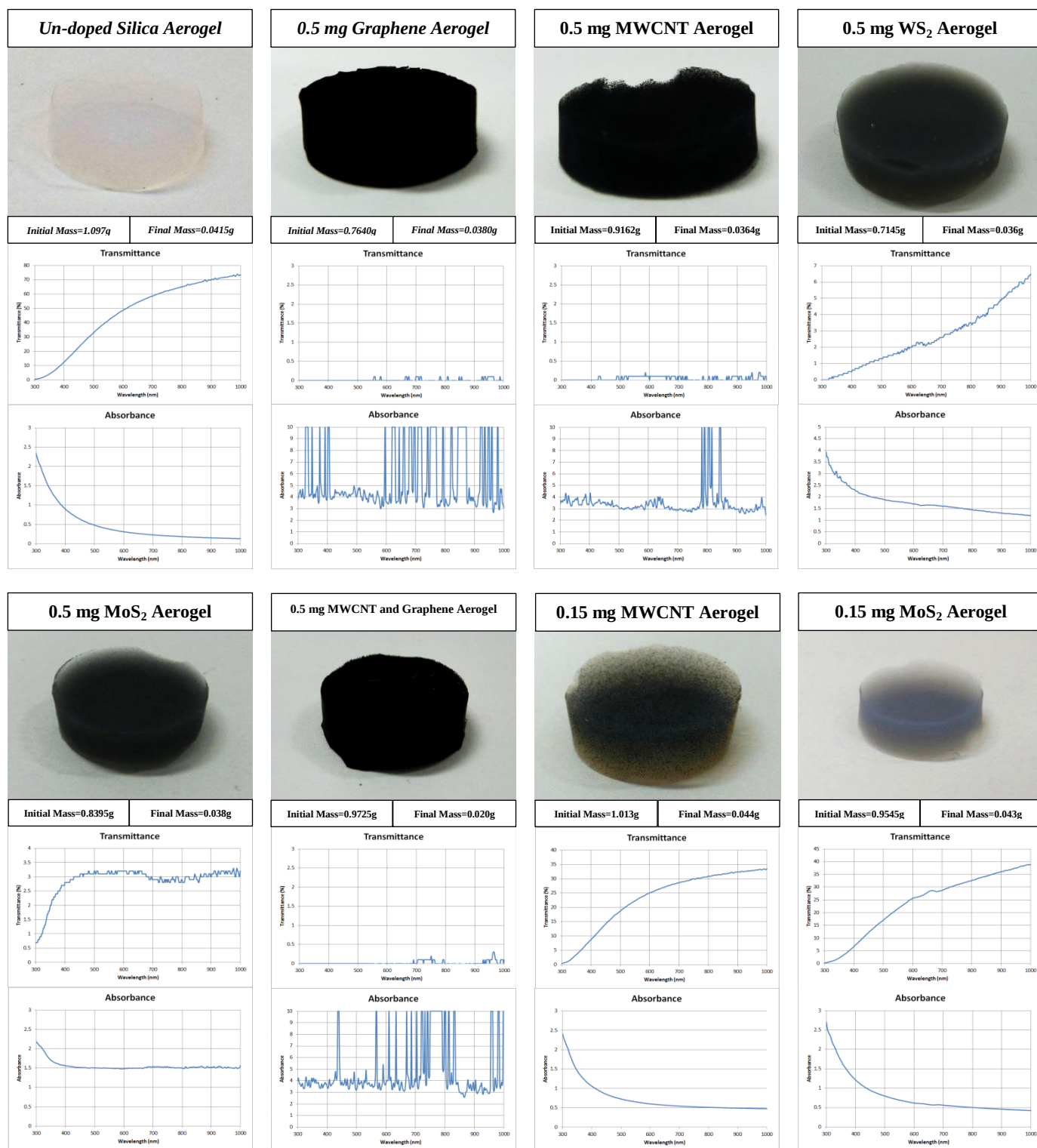


Figure 17: Visuals, masses, and optical measurements of each fabricated aerogel are shown.

Direct two-probe electrical conductivity measurements were attempted on the aerogels. Being over 90% air, it was difficult to make good electrical contact with the aerogels without damaging them. Getting any electrical measurement at all would suggest that the aerogel is electrically conducting all the way through, meaning that the aerogels can be potentially used for high surface area catalysis. A separate aerogel doped with 0.5 mg of MWCNT and graphene was prepared to have its conductivity measured. After dozens of attempted measurements, only one measurement was obtained that suggests the aerogel is conductive all the way through.

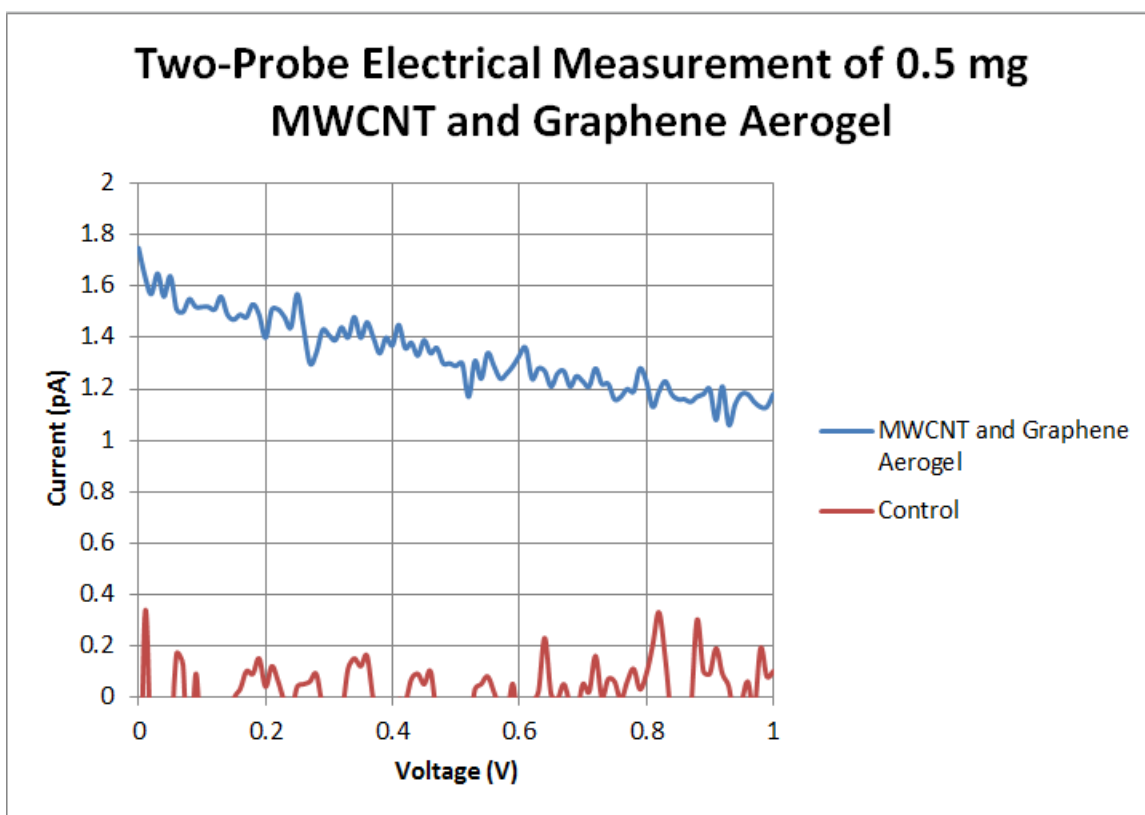


Figure 18: A current measurement on an aerogel doped with MWCNT and graphene from 0 to 1 Volts. The electrical conductivity of the aerogels is difficult to measure with our current setup. The current measurement is dubious; a better set up and more data is needed.

The sample was ultimately destroyed during the numerous measurement attempts due to the destructive nature of the two-probe measuring setup, which is manually operated. There are some interesting things to be noted from the one measurement obtained shown in Figure 18.

Firstly, there was a decrease in current as the voltage was increased, possibly due to discharge

over time. Additionally, the current observed from the two-probe measurement is in the picoamp range. It is possible that these observations are a result of the properties of aerogels. Being that aerogels are among the most porous and least dense materials known, and that the conductive dopants are likely physically held in place, it is reasonable that the current observed is in the picoamp range. It is important to keep in mind that the electrical conductivity measurements of the gels were in the microamp range; it is possible that the larger amperage measured in the gels is due to the pore liquid, ethanol, which is conductive and can transport electrons through the gel's pores. With only one successful measurement obtained from one sample, conclusions cannot be definitively made and more research is needed.

Conclusions and Future Work

The use of silica aerogels is a convenient way to structure nanomaterials such as MWCNT, graphene, WS_2 , and MoS_2 in three dimensions. The materials needed to fabricate silica aerogels, including ethanol, CO_2 , and TEOS are cheap, accessible, and relatively safe to use. The sol-gel chemistry required to make silica gels is relatively simple, and doping can be accomplished by simply dispersing dopants in the sols during the hydrolysis and condensation reactions. Density, absorbance, and catalytic activity are tunable in the fabricated doped silica aerogels.

For future work, larger aerogels should be made to demonstrate that these aerogels can be produced in bulk. In the smaller molds, adhesive forces between the sol and the sides of the mold can result in a relatively large meniscus. A larger mold would minimize the depth of the meniscus with respect to the gel diameter, resulting in a flatter aerogel. If the flatness of the aerogels can be increased dramatically, it would allow for additional characterization. The aerogels would be more easily imaged using scanning electron microscopy and their thermal conductivities would be more easily measured if the aerogels' flatness were increased.

A way to reliably measure the electrical conductivity of the aerogels should be developed. It may be possible to stick wires into the gels while they are forming. A concern with this approach, however, is that due to the gel shrinkage during supercritical drying and the likely difference in the thermal expansion coefficients between the wire and the gel, stresses can build at the interface between the gel and the wire's surface, possibly damaging the resulting aerogel. Putting conductive silver paste on the aerogel was attempted to make it easier to make good contact with the aerogel without breaking it. However, independent tests indicated that the silver paste we used was not working properly. New conductive paste should be purchased and this idea revisited.

More aerogels with varying dopant concentrations should be made to verify the correlation between concentrations and various properties such as absorbance and conductivity. A critical dopant concentration exists below which the aerogel is not conductive all the way through; this critical concentration should be found for each dopant type.

The compressive strength of each prepared aerogel will be tested using the Q800 Dynamic Mechanical Analyzer from TA Instruments® to determine if dopant has any effect on

this property. The Q800 Dynamic Mechanical Analyzer was purchased but had not been set up yet at the time of writing. The data will be acquired shortly after this report's submission and submitted to Professor Panchapakesan.

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