SYNTHESIS AND PATTERNING A NEW 1-D SEMICONDUCTOR FOR SENSORS, AND FUNCTIONALIZING THE MXene SURFACE

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In partial requirements for the
Degree of Bachelor's of Science,
B.S. in Chemistry and B.S. in Mechanical Engineering

submitted to the Faculty of
WORCESTER POLYTECHNIC INSTITUTE
100 Institute Road, Worcester, Massachusetts 01609

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Printed in the United States of America.

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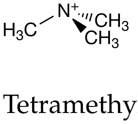
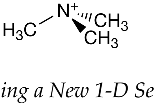
PREFACE

Quat-Derived Nanostructures (QDNs) are titanium carbide 2-D nanoflakes that are highly oxidized and air-stable. Through their synthesis, I learned that the surface is easily modifiable, making them good for inkjet printing and for further sensor applications. X-Ray Photoelectron Spectroscopy (XPS) enabled me to determine the electronic and structural properties that were changed during synthesis, as the carbon and titanium regions of the spectra reflected the oxidation that occurred. Following synthesis and XPS, I created an ink with the QDNs and completed viscosity and surface tension testing to determine the ability for future inkjet printing capabilities. I also worked on the functionalization of the MXene surface to study the electronic changes that they would produce.

ACKNOWLEDGMENTS

Thank you to Professor Lyubov Titova and her laboratory for their assistance in early QDN synthesis analysis, and thanks to everyone in Grimmgroup who assisted me in the lab and made the work seem less like a job. Thank you to Colin McNamara from Professor Pratap Rao's group for his expertise with the Rheometer and Goniometer. Thank you to Professor Rao for the opportunity to explore new mechanical properties of solvents and expand my engineering background through this project. Thank you to Julia Martin for helping me get my feet underneath me for this project, and for helping me to interpret the loads of XPS data I collected. And finally, thank you to Professor Ron Grimm for being a role model throughout my time at WPI and for mentoring me through the challenges that I faced in and out of the lab.

GLOSSARY

EtOH	Ethanol, CH_3CH_2OH
IPA	*iso*-Propyl alcohol, $CH_3CH_2(OH)CH_3$
QDN	Quat-derived nanostructure(s)
rpm	Revolutions per minute
TiC	Titanium carbide
TMA	Tetramethylammonium (cation) 
TMAOH	Tetramethylammonium hydroxide 

XPS	X-ray photoelectron spectra (generated data) *or* X-ray photoelectron spectroscopy (technique)

CHAPTER 1

INTRODUCTION AND MOTIVATION

MXenes and Quat-Derived Nanostructures (QDNs) are both titanium carbide nanomaterials that have desirable electronic properties and show promising properties of sensor and semiconductor apparatuses. They each have different strengths, so the synthesis of QDNs and the functionalization of the MXene surface were independently researched. Following the QDN synthesis, ink properties were researched and measured to determine if the QDNs would be viable for inkjet printing applications. QDNs are a recently discovered material, while MXenes have been more heavily researched. The synthesis techniques for the QDN material were based off a recent paper produced by a group out of Drexel University.[1] The ability to inkjet print a conductive material has many useful qualities such as being able to create computer chips and sensors at a faster and cheaper rate. Being able to successfully synthesize QDNs while also successfully functionalizing the MXene surface has set this project up well for someone to functionalize the QDN surface in the future, and then continue to print the material.

CHAPTER 2

BACKGROUND

2.1 QDN Background

Quat-Derived Nanostructures (QDNs) are titanium carboxide structures that form in 2-D sheets. As seen in a paper recently published from Drexel University,[1] these materials are easy to synthesize and show exceptional properties that are very applicable to electrochemistry and other conductive applications. QDNs are synthesized by combining TiC and tetramethylammonium hydroxide, $(CH_3)_4NOH$ or TMAOH, and allowed to stir at different temperatures for a few days. The materials combine, producing a dark solid that was rinsed thoroughly with water and ethanol. These materials were discovered while trying to remove features from MXenes.

2.2 MXenes and their Unique Properties

MXenes are 2-D early transition metal carbides that have conductive A element MAX phases. The layers are connected by strong covalent, metallic, and ionic bonds. These metal carbides are conductive, as well as hydrophobic, so they have a substantial amount of potential applications. The layers are mixed with carbon, titanium, aluminum, oxygen, nitrogen, and fluorine. They are hexagonal M layers with other X layers in the octahedral locations, and a layer of A layers from the etching processes. The properties of MXenes that I was interested in are their bandgaps. The many varieties of MXenes have bandgaps around 1 eV, and this makes them good at semiconducting. MXenes are inherently conductive, and because they are nanomaterials, they have applications such as electronic devices, sensors, catalysts, additives for polymers, electromagnetic storing potentials, and fuel cells.[2]

2.3 Silanes

Silanes are highly reactive molecules consisting of a silicon and a branched section that would hold different properties. Some popular ends are chlorine, fluorine, methoxy, ethoxy, phenyl or other organics.[3] In production lines, they are used as coatings, and for my project I was using silanes to see how tunable the bandgap of the MXene is.

2.4 Inkjet Printing of Semiconductors

Inkjet printing semiconductors have become increasingly popular because of the ease of printing soluble materials. The ability to control the film produced by inkjet printing is better and allows for simple thin-film formation. The control of the temperature in the loading stage as well as through the nozzle is another benefit of printing, as it allows for an array of materials to be able to be printed by the same instrument. The benefits of inkjet printing to spin coating a material is the ability to lay the material exactly where you want it.[4] Organic semiconductors have also become more popular because they have viscosities that are more compatible with inkjet printers that are available today. The organic solutions used for these semiconductors are more environmentally stable and more practical to use than past solutions for semiconductors. By using organic materials that are already very well known, the health risk is less than using a lesser-known chemical.[5] Inkjet printing semiconductors is a well-known process and doing the same with the QDN material is the next logical step.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials and Chemicals

All the chemicals I used were used as is with no alterations unless otherwise mentioned. For the QDN synthesis, the chemicals used were titanium carbide (TiC, 99%, Stream Chemicals Inc.) and tetramethylammonium hydroxide ($(CH_3)_4NOH$, 25% in water, Acros Organics). For the silane reactions, the chemicals used were ethyl alcohol (EtOH, C_2H_5OH, 200 Proof, Pharmco), Acetic Acid (CH_3COOH, 99.7+%, Acros Organics), and the silanes. The silanes used were (3,3,3-trifluoropropyl)trichlorosilane (97%, Alfa Aesar), (3,3,3-trifluoroprpyl)trimethoxysilane (97%, Alfa Aesar), and (3-cyanopropyl)tri-chlorosilane ($Cl_3Si(CH_2)_3CN$, 98%, Alfa Aesar). Other chemicals that were used for the MXene functionalization were dry toluene (>99.5%, Fisher Scientific) and isopropanol (IPA, 99.6%, Acros Organics). Finally, for my ink creation, the three solvents used were ethyl-(L) lactate ($C_5H_{10}O_3$, 97%, Acros Organic), 2-*n*-butoxyethanol ($CH_3(CH_2)OCH_2CH_2OH$, 99%, Alfa Aesar), and 1-octanol ($CH_3(CH_2)_7OH$, 99%, Alfa Aesar).

3.2 Synthesis of QDNs

The QDN synthesis was based off of the group that discovered them at Drexel.[2] The group there performed synthesis at varying temperature for varying times. They tested reactions between room temperature and 80 °C, and anywhere from three to ten days. I created a plan to synthesize QDNs at 50 °C and 80 °C for three, five, seven, and ten days at each temperature. I did this to discover which synthesis procedure would produce the best QDN. While I could not find evidence to support if certain synthesis were better than others, I found that three days at 80 °C was sufficient at creating QDNs.

Each reaction done was set up with one gram of TiC powder and ten grams of tetramethyl ammonium hydroxide in a plastic bottle with stir bars inside. The bottles were then placed on a hot plate set at either temperature (50 °C or 80 °C), turned on to spin at a medium speed, and then left alone for the set number of days (three to ten). After the cooking, the material was taken off the hot plate and the post synthesis washes were completed. The material was transferred from the plastic bottle into a centrifuge tube, and then five washes of ethanol were completed by filling in an arbitrary amount of EtOH and putting it into a centrifuge for two minutes at 3900 rpm. The excess liquid was removed, leaving a solid clump of QDN at the bottom of the tube. Then, two water washes were done in the same manner, and the water was saved, as the QDN was suspended in it, in a separate centrifuge tube. The solid at the bottom was also saved.

3.3 Functionalization of MXenes

The original procedure for attaching the chosen silane to the MXene surface was to prepare the MXene and the silane solution separately. The MXene prep was four grams of EtOH, one gram of degassed H_2O, about 0.1 g of MXene powder, and two mL of pH four acetic acid. These were added to a three-necked round bottom flask and sonicated for about thirty minutes to fully incorporate them. The silane preparation was done in a flush box as the silanes are all somewhat air and water sensitive, so they are stored in the flush box to minimize their exposure. The silanes were prepped in five mL of EtOH and 200 μL of the chosen silane. Then the MXene was put over a stir plate with a stir bar and was flushed with argon. This argon flow continued for the whole reaction to continuously flush the system. The silane was loaded into a syringe and added slowly over two hours. I added about half a millimeter every fifteen to twenty minutes, and then let the reaction run for a total of eight hours. This was then rinsed in a similar manner to how the QDNs were rinsed. The silanized MXenes were rinsed with EtOH in a centrifuge tube. The product was spun at 3900 rpm in a centrifuge for two minutes, five times over. I did this for all of the silanes listed above. They were either in EtOH or dry toluene, depending on the silane. An image of this initial set up is seen in Fig. 3.1. The second way I silanized the MXene surface was using an apparatus glass blown in-house by Grimm. It can be seen in Fig. 3.2. This fixture would mount onto a dram vial and would pose significantly less oxidation risk to the presilanized MXene. The silane set up process was done in the dram vial and then extracted into a syringe to allow the glassware to be silanized before the MXene solution was added. Then the MXene solution was made in the flush box, using the same amounts as previously mentioned. The MXene was transferred quickly into the silanized dram vial, and then closed off to the air. Immediately, a flow of nitrogen was released through the two side ports. The nitrogen would be a strong enough

Figure 3.1 The initial set up of the MXene surface silanization, with inlet of Argon on the right arm, Argon outlet on the left arm, and the silane syringe in the center. The stir bar is present in the three-neck flask, and from this distance the stir bar would mix the solution.

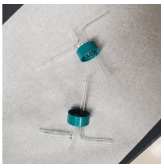


Figure 3.2 Glassware created in house in order to minimize oxidization of the MXene before silanization is achieved.

flow to disrupt the MXene solution. Then the silane was added through the top port every fifteen to twenty minutes as previously done and allowed to bubble for eight hours. Some experiments lasted only six hours which resulted in less silanes on the surface after XPS.

3.4 Creation of the Ink

The ink was created using the solvents listed above and dried QDN. The QDNs were dried from their original solvents with a rotavapor, and then added to the solvents. The original QDN solvent was rotovapored for about twenty minutes to remove the water, and then the dried QDN was removed from the round bottom flask and added to a centrifuge tube. The chosen solvent was then added, and the solution was sonicated for about thirty minutes to create a thorough mixing. While the QDN does not dissolve in the solvent, it does mix evenly so an even print could be produced.

3.5 Preparation of QDN/MXene for XPS

Sludge from the QDN was loaded onto the puck with a glass pipette, and the MXenes were deposited in a similar manner. The puck was polished with 1200 grit sandpaper and rinsed with soap water, then water, and then isopropanol. The samples were deposited directly onto the polished puck.

The puck was placed in a vacuum oven for anywhere between two hours and overnight, and then the puck was pumped into the instrument for two to three hours. Once it was at the correct pressure and the sample was thoroughly degassed, it was loaded into the main chamber and the data was collected.

3.6 X-ray Photoelectron Spectra

All of the samples for XPS were collected in a PHI 5600 multitechnique system. The system has been previously described.[6] The PHI 5600 system is from a third-party data acquisition system. The analysis chamber is kept at a pressure of about 1×10^{-9} torr. The X-ray photoelectrons were collected with a hemisphere energy analyzer. The monochromated Al Kα source produces the X-rays with a 90° angle with respect to the takeoff angle of the energy analyzer. For these experiments, the XPS used the puck as the sample angle and that allowed for a 45° angle for the incoming monochromatoed X-rays as well as the photoelectron takeoff angle. My X-ray photoelectron acquisitions were done on wide energy survey scans and included high resolution scans of the C 1s, O1s, Ti 2p, and theN1s regions of the QDN samples, and the MXene samples included Si 2p and F 1s regions as well as the ones stated previously. The peaks were quantified using a LabVIEW program on published spectra.[7] The data was fit using emission-baseline-corrected functions where x was nonlinearly scaled from a pure Gaussian (x=0) to a pure Lorentzian (x=100). The peaks with many peaks in one spectral region were restrained to identical fill-width-half-maximum values.

3.7 Rheometer Testing

The Rheometer was used to test the viscosity of the inks. First, one turns it on, checks the air supply, and opens the software. The electronics circulator should be checked, and then the cone shaped attachment was inserted to the tip so that it could rotate freely. Once the software was loaded, the geometry of the tip was checked, and the gap between the solvent plate and the tip was zeroed. Once this was completed, the ink could be added to the solvent plate and the geometry gap should be achieved. The excess solvent should be cleaned, and then the experiment can be started.

3.8 Goniometer Testing

The Goniometer was used to collect surface tension data. The Goniometer is more complex for the user, but the software is easier. First, the software *Drop Image Pro* should be loaded. The light on the instrument should be turned on, and the camera lens cover should be removed. The ink is prepared by loading the needle with the ink. It is then inserted into the holding apparatus and the needle is lowered until it is visible on the camera used in the software. The correct solvent is selected on the software and the camera is adjusted so it is sharp on the needle. Once the needle is focused, a drop is hand ejected from the needle, but only to the point where the droplet is hanging from the end of the needle. The surface tension can then be measured.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 QDN Synthesis

The XPS data seen in Fig. 4.1 shows the spectra of the TiC powder as well as the spectra of the fully synthesized QDN. The bottom spectra shows the TiC powder pre-synthesis. As seen, there is no nitrogen peak, as well as a TiC doublet on the titanium region at about 454.5 and 461 eV. Post synthesis, the TiC doublet disappears as the TiC changes into TiO at the surface. While there is TiO present in the initial TiC spectra, this is because oxygen from the air reacts on the TiC surface. The nitrogen peak also grows, which indicates that there is some leftover starting material on the surface of the QDN. The tetramethylammonium hydroxide was not completely removed from the surface from the post synthesis washes, but the carbon peak is largely from the oxidized carbon on the surface. The oxygen peak also increases slightly due to more oxidized carbon on the surface.

4.2 Functionalization of MXene

Based on the XPS that was collected, I was able to successfully functionalize the MXene surface. In Fig. 4.2, I show the non-functionalized MXene surface in order to compare it with the functionalized surface. Without such comparison, there would be no viable way of understanding whether or not the silanes had stuck to the surface. For example, Fig. 4.3 shows the (3-3-3-trifluoropropyl)trichlorosilane on the surface of the MXene. I can determine that the silane is bonded to the surface of the MXene because the increase of the far left carbon peak, as well as the second doublet in the titanium region. The left most fluorene peak also grows, and this is because of the fluorene that is on the silane. There is originally fluorine in the MXene structure because

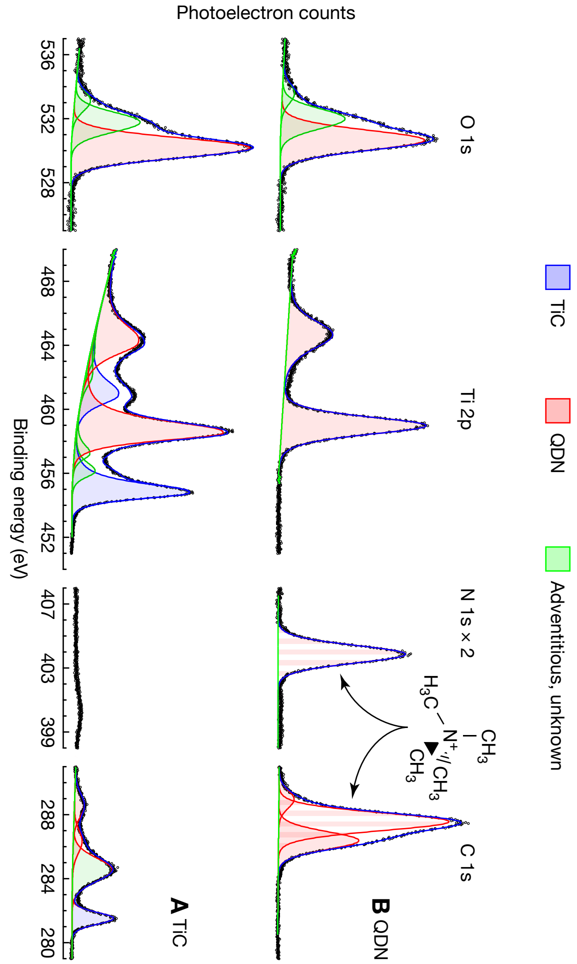


Figure 4.1 This is the XPS data of the starting material TiC vs the synthesized QDN material.

of HF washes that were done during the MXene synthesis. The nonfunctionalized MXene came into contact with oxygen at some point during the pre-reaction set-up, as the titanium region shows a lot of oxidation. There should not be any oxidation in the non-functionalized MXene. After we discovered how easily the MXene oxidizes, we took more care when transferring the MXene solution into the reaction vessel. The other silanes on the MXene surface can be seen in the Additional Materials, Chapter 6 of this paper.

4.3 Ink Results

The more successful of the two inks I produced is the one with an ethyl-(L) lactate solvent. See Fig. 4.4 for viscosity data and Fig. 4.5 for surface tension data. Based on the results received, both of these inks are within the physical ranges of the printer. Based on the manual for the printer available, the viscosity range is being within two and thirty centipoise, and the surface tension needs to be around thirty dynes/cm. The data for the ethyl-(L) lactate + QDN solvent showed to be well within range for both of these physical properties. For the 2-*n*-butoxyethanol solution, it also showed similar properties as the ethyl-(L) lactate solution, although QDN visually suspended better in the ethyl-(L) lactate than the 2-*n*-butoxyethanol. While the octanol solution did lead to the QDN being suspended, it was poor and would fall through the solution soon after holding the vial still. The data collected for the ink production shows that I successfully created an ink that could be used in the inkjet printer. The solvents used held the correct properties on their own, and when the QDN material was added it did not affect the values greatly, so they would be viable for printing. See the additional graphs of the other ink solutions in the Additional Material section. The graphs in that section show that the 2-*n*-butoxyethanol have good properties to be a successful ink, but they do not fit the qualifications as well as the ethyl-(L) lactate solutions do. When the QDN is added to the 2-*n*-butoxyethanol, something strange happens in the surface tension measurements. While the reason for the strange pattern in Fig. 6.8 is unknown, it is believed that the ethyl-(L) lactate solution was a better fit. You can also compare the ethyl-(L) lactate data in Fig. 6.3 and Fig. 6.4 to the solution with QDN to see that the values do not drastically change with the addition of the QDN.

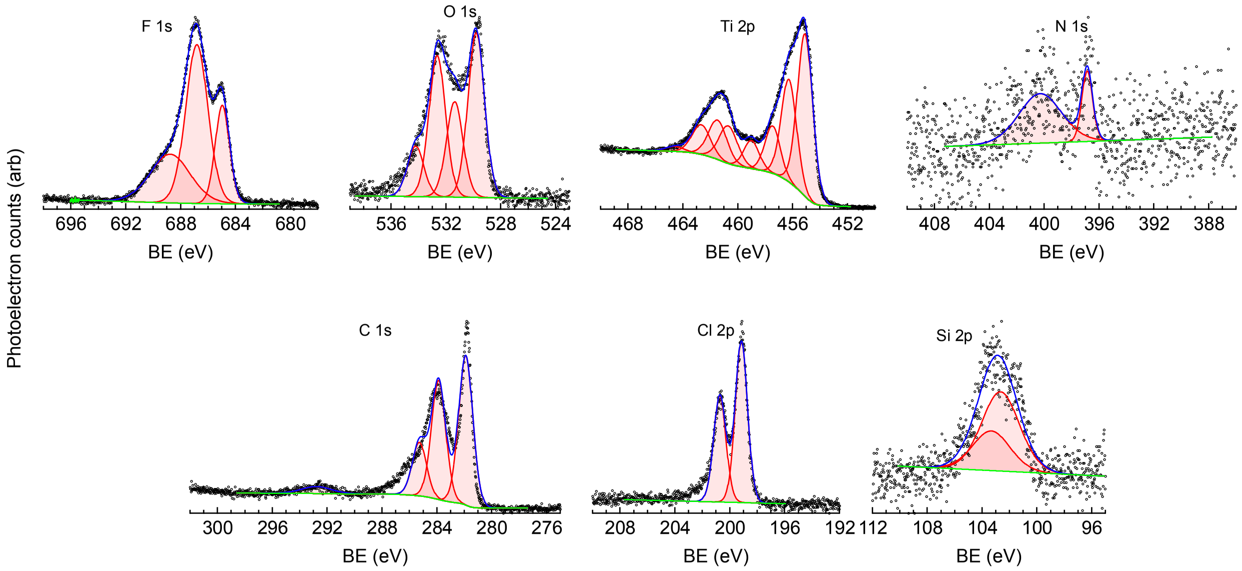


Figure 4.2 This is the non-functionalized MXene surface.

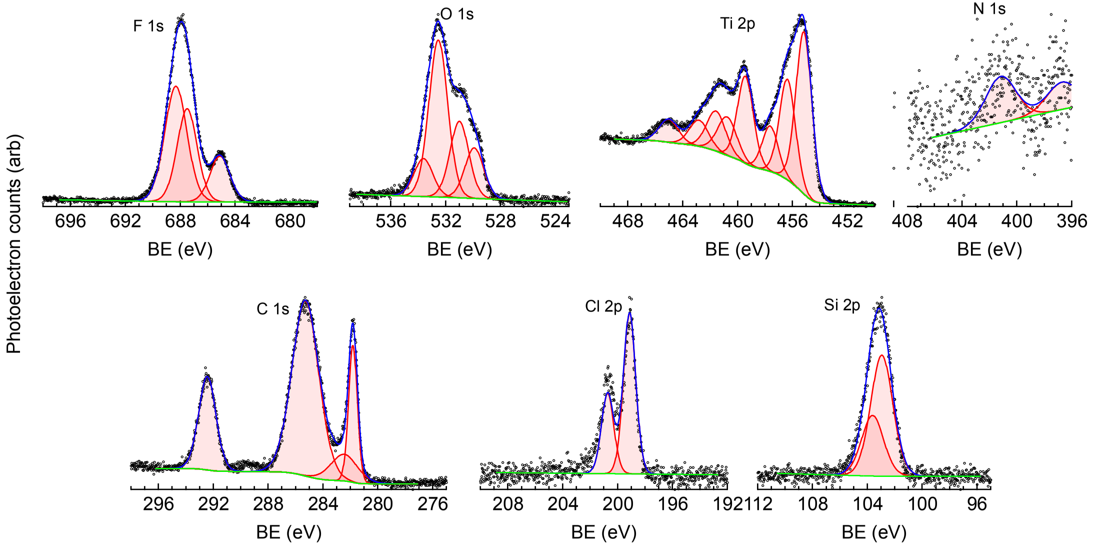


Figure 4.3 Silanized MXene surface with (3-3-3-trifluropropyl)trichlorosilane.

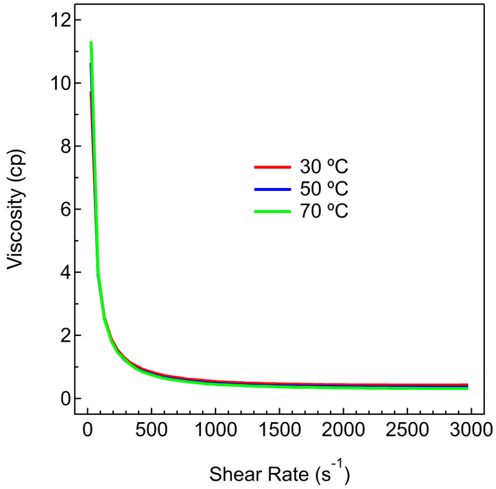


Figure 4.4 Viscosity Curve for Ethyl-(L) Lactate + QDN.

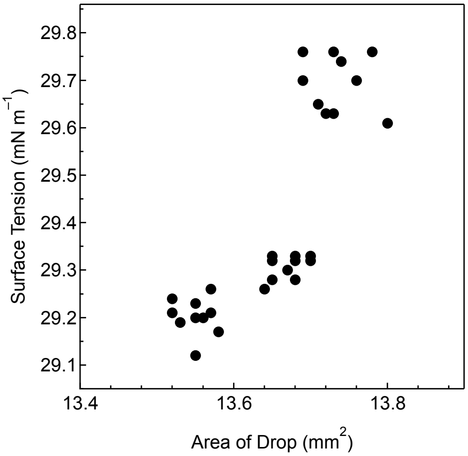


Figure 4.5 Surface Tension of Ethyl-(L) Lactate + QDN.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 QDN

In conclusion, I was able to synthesize the QDNs in a quick and efficient way, in a one pot mixture that would be easily scalable for larger production. After seeing the bandgap of the QDN, the next step would be for another student to functionalize the surface of the QDN similarly to the process I used with the MXenes. I think if the QDN bandgap can be manipulated by silanization similarly to the MXene bandgap, it could be very interesting for the sensor world. It would also be interesting to do XPS on some of the samples originally made, to see what happens to the QDN after a period of time. Observing the changes of the QDN long term could be beneficial for future uses.

5.2 MXene

I successfully functionalized MXene surfaces with a number of different silanes and was able to see the bandgap changes affected by these silanes. Using XPS I could see that the silanes were on the surface and using UPS the electronic property changes were visible. The future work that could be done on this project would be to try different silanes, such as phenyl silanes or aromatic silanes. There are some more silane materials available in the laboratory, and further experimenting with those would be a great next step. Also, using more UPS to quantify the bandgap changes would be good, so libraries of these could be collected. Finding ways to expedite the silanation process would also be interesting as an eight-hour experiment is a bit tedious. Exploring how acidic conditions affect the functionalization would also be something to look into.

5.3 Ink

Two of the three solvents I chose to create the ink are viable for ink jet printing of QDNs. They both showed the correct viscosity and surface tension properties based on the recommended values from the printer manufacturer, so theoretically they could be printed. A future student could also work to combine the solvents to create an ink that would incorporate the QDN better. A future student could also work to create an ink that is more viscous, so it falls a bit more within the properties required for the printer. I also think it would be interesting for a student to print the ink in the future to see how the QDN lays down on a substrate. To successfully print the material and observe its printed qualities would be a good step into creating a product that could be used for computer chips or sensors.

CHAPTER 6

ADDITIONAL MATERIALS

6.1 Additional QDN information

When getting samples of the QDN's ready to be analyzed by physics, the way that I prepared the QDN was on a piece of glass, and I would add it dropwise until I had reasonable layer that was opaque. I would anneal it on a hot plate at about 80 °C to ensure it would stick. Then the samples were ready for the physics department.

6.2 Additional MXene XPS

The following XP spectra represent the results of silane-functionalized MXene not presented above.

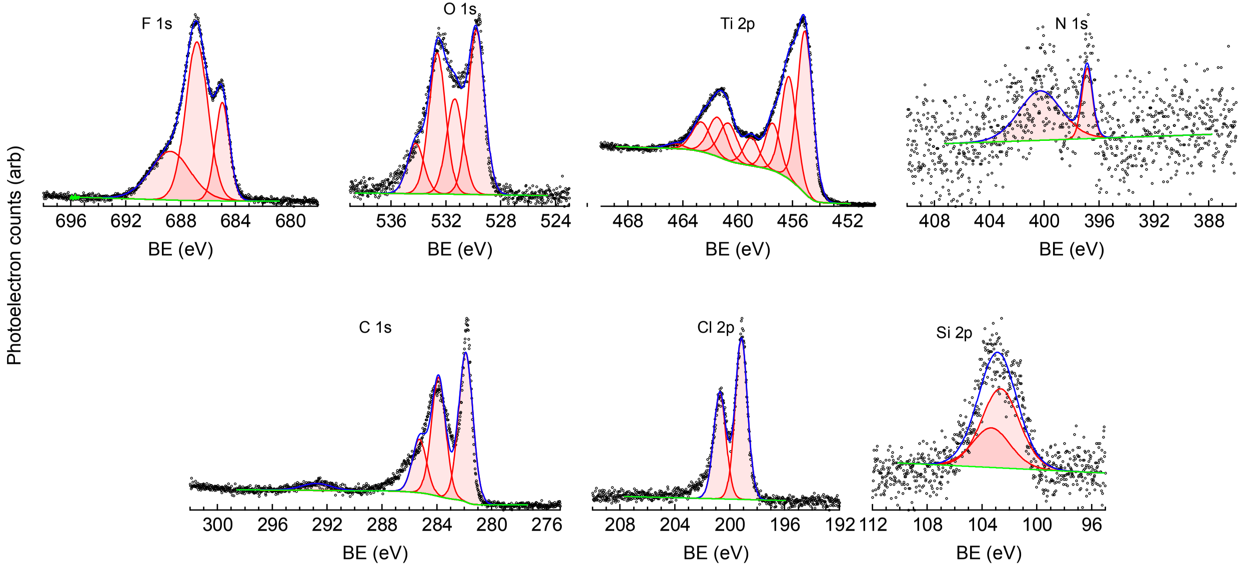


Figure 6.1 This is the XPS data of (3-3-3-trifluoropropyl)trimethoxysilane on the MXene surface.

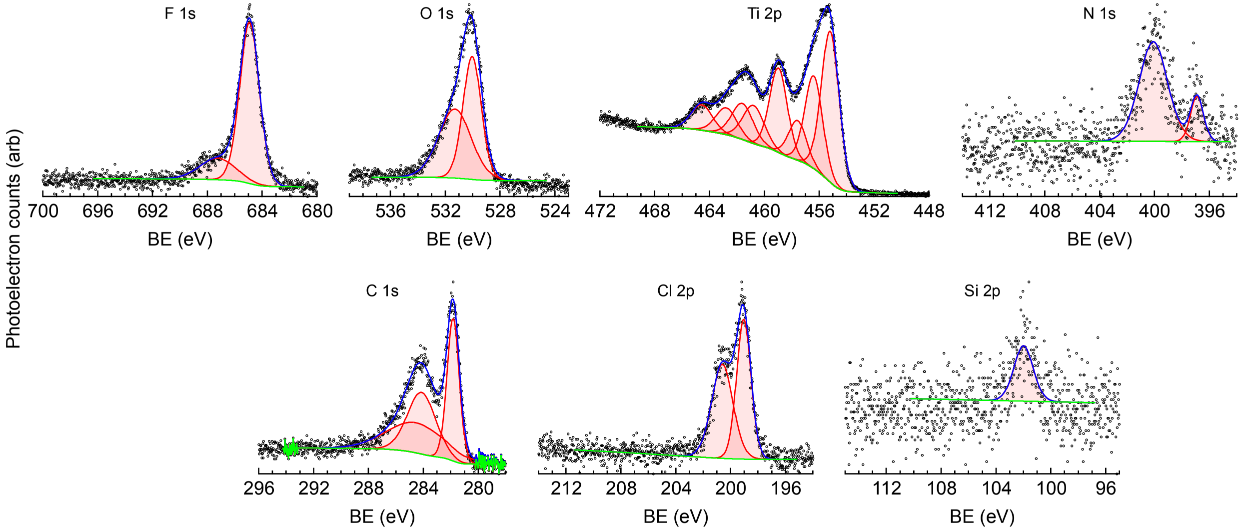


Figure 6.2 This is the XPS data of (3-cyanopropyl)trichlorosilane on the MXene surface.

6.3 Additional Ink Analysis

Based on the data collected below, I concluded that the ethyl-(L) lactate was the better solution of the two I measured. The 2-*n*-butoxyethanol + QDN mixture did something strange, where the surface tension could not be re-measured, and it would be beneficial in the future to test this.

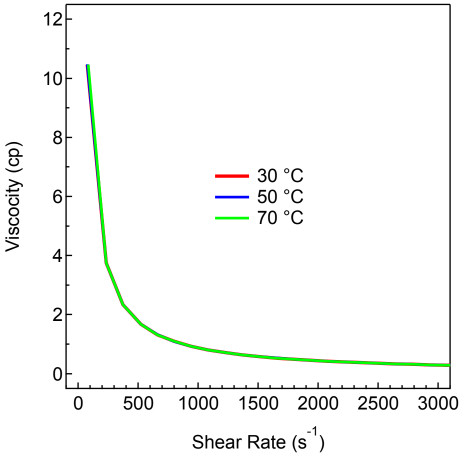


Figure 6.3 Ethyl-(L) Lactate Viscosity Measurements.

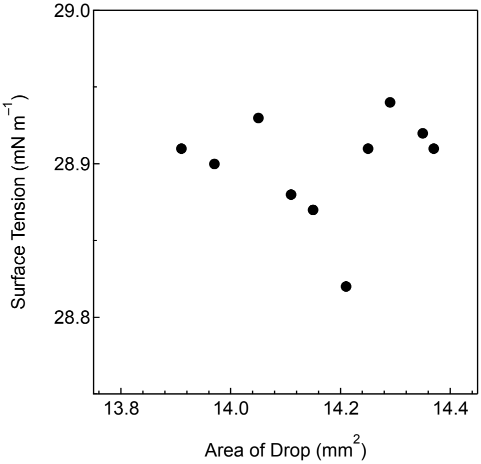


Figure 6.4 Ethyl-(L) Lactate Surface Tension Measurements.

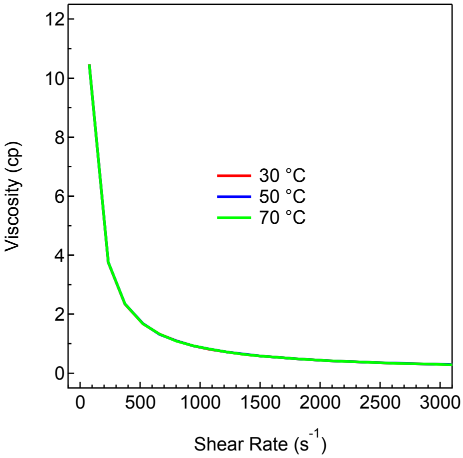


Figure 6.5 2-*n*-Butoxyethanol Viscosity Measurements.

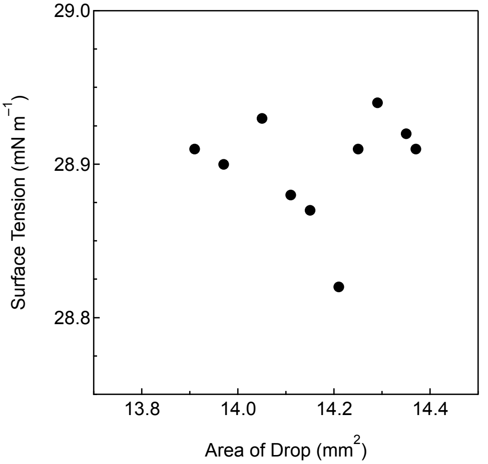


Figure 6.6 2-*n*-Butoxyethanol Surface Tension Measurements.

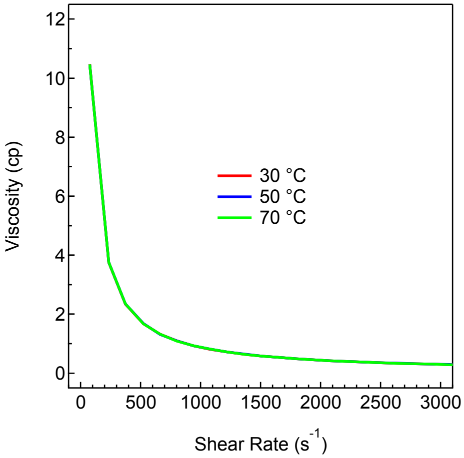


Figure 6.7 2-*n*-Butoxyethanol + QDN Viscosity Measurements.

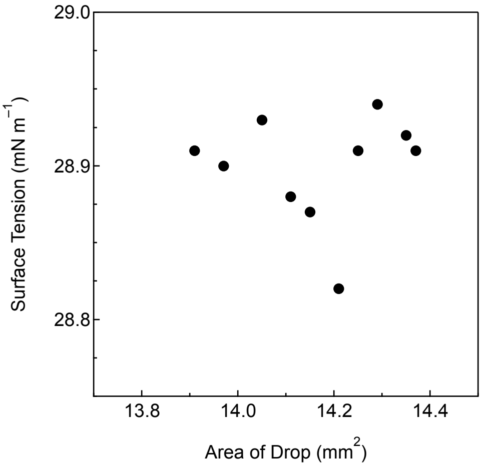


Figure 6.8 2-*n*-Butoxyethanol + QDN Surface Tension Measurements.

CHAPTER 7

REFERENCES

1. Badr, H. O., et al., Bottom-up, Scalable Synthesis of Anatase Nanofilament-Based Two-Dimensional Titanium Carbo-Oxide Flakes. *Mater. Today* **2022**, *in press*.
2. Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y., 25th Anniversary Article: Mxenes: A New Family of Two-Dimensional Materials. *Adv. Mater.* **2014**, *26*, 992–1005.
3. Witucki, G. L., A Silane Primer: Chemistry and Applications of Alkoxy Silanes. *J. Coatings Technol.* **1993**, *65*, 57.
4. Chung, S.; Cho, K.; Lee, T., Recent Progress in Inkjet-Printed Thin-Film Transistors. *Adv. Sci.* **2019**, *6*, 1801445.
5. Yoon, C., Much Concern but Little Research on Semiconductor Occupational Health Issues. *J. Korean Med. Sci.* **2012**, *27*, 461–464.
6. Carl, A. D.; Kalan, R. E.; Obayemi, J. D.; Zebaze Kana, M. G.; Soboyejo, W. O.; Grimm, R. L., Synthesis and Characterization of Alkylamine-Functionalized Si(111) for Perovskite Adhesion with Minimal Interfacial Oxidation or Electronic Defects. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34377–34388.
7. Peak Fitting in XPS. CasaXPS. accessed Aug. 2021
8. Materials Printer & Cartridge DMP-2800 Series Printer & DMC-11600 Series Cartridge 2008.