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Effect of salt on the self-assembly of amphiphiles within topological defects of nematic solvents

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ABSTRACT: Research regarding topological defects in nematic solvents is motivated by the recent discovery that they can be used as a versatile source of templates for the fabrication of organic nanostructures. In this paper we explore the influence of salts on the self-assembly of amphiphiles in defects formed in nematic solvents. The presence of salt can influence the process of molecular self-assembly within the nanoscopic environments defined by the topological defects formed in nematic solvents. To study this, we utilized fluorescence microscopy to investigate the critical aggregate concentration (CAC) of amphiphiles within topological defects in nematic solvents in the presence and absence of salt.

Introduction

Liquid crystal is a thermodynamic stable phase characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice, generally lying in the mesophase this is the temperature range between the solid and isotropic liquid phase³. The wide range of the commercial application of liquid crystals include calculators, digital watches, and computer displays. Topological defects occur in a wide variety of nature at all scales of physical systems, ranging from soft matter to quantum systems, cosmology, and thin magnetic films. The study of topological defects helps in biological systems, where they play a major role in biological cells budding and fission process ¹. In context of liquid crystals, topological defects are nanoscopic regions where the orientational order is different compared to the bulk. In this paper, we focused on the study of selfassembly of amphiphiles within defects formed in nematic liquid crystals. We do so by measuring the CAC at which the amphiphiles exhibit selfassembly. In this study we will be using nematic solvents which are the simplest class of liquid crystals. In a nematic mesophase molecules orient in a long-range order with molecular long axes aligned along a preferred direction.



Figure 1: Molecular arrangements in liquid crystalline mesophases. In a nematic mesophase, molecular orientations are correlated, while molecular positions are not. The average orientation is termed a director, n. In a cholesteric mesophase the average molecular orientation twists through the medium with a certain periodicity, while positions of molecules are not correlated. In a smectic A mesophase molecules lie in planes. Molecular axes are perpendicular to these planes but otherwise are not ordered within the planes. Smectic B has a hexagonal packing of molecules in the planes, while in smectic C the director is tilted in the planes. Columnar mesophases are often formed by disc-shaped molecules. The most common arrangements of columns in two-dimensional lattices are hexagonal, rectangular, and herringbone. In the herringbone mesophase molecules are tilted with respect to the columnar axis³.

Experimental Section



Figure 2: 4-cyano-4"-pentylbiphenyl(5CB).



Figure3:PentylcyanobiphenylDimethyloctadecyl[3-trimethoxysilylpropyl]ammonium chloride(DMOAP).



Figure 4: Molecular structures of BODIPYamphiphiles.4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (BODIPY). Figure 5: Tetra butyl Ammonium Bromide.

Materials

Tetra butyl Ammonium Bromide, Ethanol, 4cyano-4"-pentylbiphenyl(5CB),

Br⁻

Dimethyloctadecyl[3-

trimethoxysilylpropyl]ammonium chloride (DMOAP),chloroform,4,4-difluoro-5,7-dimethyl-4-bora-3a,4a-diaza-s-indacene-3-pentanoic acid (BODIPY-C5), 4,4-difluoro-5,7-dimethyl-4-bora-3a,4a-diaza-s-indacene-3-dodecanoic acid, (BODIPY-C12).

Preparation of DMOAP-Functionalized Glass Slides and Copper Wires. 1% v/v DMOAP solution was prepared by adding 100mL of deionized water with 1ml 60% v/v DMOAP. The glass slides and copper wires were incubated into the DMOAP solution for 2 hours and then sonicated for 10 mins at a 5min interval. The glass slide and copper wire were bulked rinsed with deionized water 4x and ethanol 4x, then rinsed individually with ethanol and dried under 208 nitrogen gas. Preparation of Mixtures of **BODIPY**amphiphiles and 5CB. The following procedure was used in the preparation of BODIPYamphiphiles,5CB and salt. To begin with, 1.75µl of 0.1mg ml⁻¹ BODIPY-amphiphiles in ethanol was added to 30µl of chloroform. Then 50 µl of 5CB was added to the solution. The mixture was then dried under vacuum at 45-50°C for 3 h to remove the ethanol and chloroform. The mixture of BODIPY-amphiphiles was kept in the isotropic phase before injecting into a functionalized optical cell.

Preparation of Mixtures of BODIPYamphiphiles,5CB and Tetra butyl Ammonium **Bromide.** The following procedure was used in the preparation of BODIPY-amphiphiles and 5CB. To begin with, 1.75μ l of 0.1mg ml^{-1} BODIPYamphiphiles in ethanol was added to 30μ l of chloroform. Then, 49.375μ l of 5CB and 0.625μ l(250μ M) mixture of 5CB and Tetra butyl Ammonium Bromide was added to the solution. The mixture was then dried under vacuum at 45-50°C for 4h to remove the ethanol and chloroform. The mixture of BODIPY-amphiphiles was kept in the isotropic phase before injecting into a functionalized optical cell.



Figure 6: Experimental setup used to generate m = -1/2 defects; an optical cell consisting of surface-functionalized copper wires and glass substrates. Cross section of (D) in the *yz*-plane, showing a pair of m = -1/2 disclinations formed in the confined nematic LC. The dashed lines show local ordering of the mesogens and the red dots represent the cores of the disclinations².

Fabrication of optical cells. Optical cells were prepared by pairing two DMOAP-Functionalized coated glass slides and spacing them apart with two DMOAP-functionalized copper wires. The two surfaces of the cell were put tighter using a clip. The mixture of the BODIPY-amphiphiles and 5CB in the isotropic phase was introduced into the optical cell and then cooled to the nematic phase at room temperature(21-22°C).

Fluorescence Microscopy of BODIPYamphiphiles in Nematic 5CB. The distribution of BODIPY-amphiphiles in 5CB was characterized by inverted fluorescence microscopy using Olympus IX71 microscope equipped with a mercury lamp. Images were acquired with a camera controlled by an imaging software. The following fluorescence filters were used: Filter 1 was used to characterize the monomer signal and consisted of an excitation filter transmitting light at 457–502 nm(λ^{ex} :457-502nm) and emission filter transmitting light 510-562nm(λ^{em} :510-562nm). Filter 2 was used to characterize the dimer signal and comprised pf an excitation filter transmitting light at 533-584nm(λ^{ex} :533-584nm) and emission filter transmitting light at 606-684nm(λ^{em} :606-684nm).

Quantification of fluorescence intensity. The fluorescence intensity of the BODIPY-amphiphiles were quantified from images using ImageJ software. A region of the liquid crystals adjacent to the defect line for quantification of the fluorescence intensity of the liquid crystal.



Figure 7: Self-assembly of amphiphiles in LC defects. a-h(left to right): a-b BODIPY-C5 (40µM), c-d BODIPY-C5(50µM), e-f BODIPY -C12(40µM) and BODIPY C12(50µM).

Results and Discussion

To begin with we characterized the interaction of BODIPY conjugated to an amphiphile with chain length:C5 and C12 with a -1/2 defect in 5CB nematic solvent. We focus here on the results obtained using BODIPY C-12. The defect line was observed using bright-field optical imaging as shown in fig 7. For concentrations of BODIPY-C12 up to 20µM, independent of the excitation/emission wavelengths used for imaging measured no difference we between the



Figure 8: a) 10 μM BODIPY-C12 @500 μM TBABr, b) 30 μM BODIPY-C12, 500 μM TBABr.

fluorescence intensity and the bulk liquid crystals. When the concentration of BODIPY-C12 was greater than 20μ M the fluorescence in the dimer became more intense than that in the defect relative to the bulk of the liquid crystals. This observation was only in the dimer fluorescence signal and not in the monomer signal. These results indicate that BODIPY C12, beyond a critical assembly concentration (CAC) of 20μ M, assembles within the defect environment while remaining singly distributed in the bulk of the liquid crystal.

Next the interaction of BODIPY conjugated to an amphiphile in the presence of salt, Tetra Butyl Ammonium Bromide (TBABr), was observed. At high concentrations of salt the formation of singular line defect was disrupted as shown in fig 8. When 500 μ M of TBABr was used, the defects didn't form. This could have occurred due to the presence of salt which disrupts the LC ordering in the system. After trying different concentration of salt, we found that at 250 μ M TBABr defects were formed.



Figure 9: Self-assembly of amphiphiles in LC defects. a-h (left to right): a-b BODIPY-C12(40μ M), c-d BODIPY-C12(40μ M)and 250 μ M TBABr, e-f BODIPY -C12(65μ M) and BODIPY C12(65μ M) and 250 μ M TBABr.

Based on the results in fig 9. At amphiphile concentrations lower than 40 μ M, fluorescence signal was observed in the BODIPY amphiphiles in the absence of salt but no emission was recorded in the presence of salt. At higher concentrations, greater than 40 μ M, the fluorescence intensity in the presence of salt was detected. This indicates that addition of salts delays the onset of amphiphile assembly in the defects. We hypothesize this to be an outcome of the change in LC ordering in and around the defects. The presence of salts can increase the disorder in the bulk nematic phase which can lead to a decrease in the driving force for amphiphile assembly within the defects.



Figure 10: Fluorescence intensity of BODIPYamphiphiles (C12) BODIPY-C12: in defect (squares); BODIPY-C12 and TBABr: in defect (up triangles). To end this (fig) shows the CAC on BODIPY-amphiphiles and BODIPY-amphiphiles in the presence of salt. CAC of BODIPY-amphiphiles increases in the presence of salt.

Overall, the results presented in this paper answers our question that the presence of salt disrupts the local nano environment created by singular topological defects formed in nematic liquid crystals. We also report that salts can delay the assembly of amphiphiles within the defects. This is in contrast to studies in aqueous systems, where the inclusion of salts typically increases the tendency of amphiphiles to form assemblies. Along with the fundamental understanding of the effect of salts on amphiphile assembly, this finding expands the potential utility of defects as nanoreactors in systems with salt. Future efforts will seek to use ionized salts as opposed to organic salt used in this study. In addition, the influence of the salts on the molecular assembly of polymers will also be investigated.

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Desymmetrization of Meso Diols using Aminoxyl Radical Catalysts

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ABSTRACT: Chiral lactones serve as building blocks for a multitude of purposes in organic chemistry. Specifically, as precursors and monomers for pharmaceutical drugs and other synthetic materials used in industry. By employing chiral peptide-based catalysts as well as utilizing electrochemistry we are presenting a new and more efficient way for synthesis paths. We have obtained moderate to high enantiomeric excess with a variety of substrates. Ongoing efforts will be to broaden the substrate scope as well as the catalysts reactivity site.

Introduction

Chiral lactones serve as versatile building blocks in material science and in pharmaceuticals. They are also one common motif in active pharmaceutical ingredients and can be used in a variety of industries: cosmetics, food production, etc. In organic chemistry, diols serve as building blocks for further synthesis. They easily aid the conversion between different functional groups. The desymmetrization of meso compounds, specifically in our case diols, has become a very popular and effective route to asymmetric synthesis. Enantiomers can behave differently with a single compound. The desymmetrization of compounds and isolating one enantiomer for further synthesis allows us to control how the desired product behaves. In oxidizing the meso diol to the chiral lactone several synthesis paths become available.

Catalytic oxidative desymmetrization of meso diols has been previously studied by Bobbitt.¹ They discovered the first asymmetric electrocatalytic oxidation of diols to chiral lactones using a SPIROXYL-modified graphite felt electrode. More recently, Iwabuchi's oxidative kinetic resolution of secondary alcohols is another form of alcohol oxidation, now with the use of a chiral catalyst.² Notably, it is the first example applicable to various unactivated aliphatic secondary alcohols; but the catalyst synthesis is 14 steps which can be cumbersome.

We envisioned that a modular platform for asymmetric alcohol oxidation would enable easier synthesis and allow for expansion to a more challenging substrate scope. By using a chiral peptide-based catalyst we are providing a more efficient route to obtaining a chiral lactone product. Our catalysts are highly modular, meaning we are easily able to optimize the catalysts to react with our meso diols. Aside from being modular, the peptides are easy to synthesize. Once our platform is created, the peptides can be easily optimized for specific use in industry and can be used for many different types of chemistry.

Another innovation is our use of electrocatalysis. Instead of using chemical oxidation we are able to limit the production of side products. This technique also provides us with theoretical insight. We are able to do different types of mechanistic studies by going from a chemical to an electrochemical driving force. Electrochemistry also offers a greener method to synthesis. Although we are not currently focused on this aspect, this may be looked at in the future.

Substrate Synthesis

Synthesis of (4R,5S)-1,3-dibenzyl-4,5bis(hydroxymethyl)imidazolidin-2-one

Thionyl chloride (4.93 mmol, 1 eq) was added dropwise to a solution of 1,3-dibenzyl-2-oxoimidazolidine-4,5-dicarboxylic acid (19.75 mmol, 4 eq) in methanol cooled with water. The mixture stirred at 40°C for 21 hours. An additional equivalence of thionyl chloride was added with three drops of DMF and reaction continued to run for 3 more hours. Air was then blown on top of the vessel to evaporate HCl. A drop of water was then added to the vessel and the product crashed out. Solution was then vacuum filtered, and solids were washed with cold methanol then collected and dried on high vacuum to give Dimethyl (4R, 5S)- 1,3-dibenzyl-2-oxoimidazolidine-4,5-dicarboxylate.³ This was then reduced by standard LAH procedure to give (4R,5S)-1,3-dibenzyl-4,5-bis(hydroxymethyl)imidazolidin-2-one.

Synthesis of ((9R,10R,12S)-9,10-dihydro-9,10-ethanoanthracene-11,12-diyl) dimethanol

Maleic anhydride (2.18 g) and Anthracene (4g) were added to a round bottom flask with 100 mL of Toluene and reacted at room temperature for 6 hours. After cooling to room temperature, the solvent was removed in vacuo to yield a white powder which was purified by recrystallization from DCM: Ether (60:80) to give (9R,10R,11S)-9,10-dihydro-9,10-[3,4] furanoanthracene-12,14-dione (11.22 mmol, 1 eq)⁴ which was then dissolved in 9.35 mL of dry THF was added to a dry round bottom flask under nitrogen. 28.06 mL of dry THF was then added and LAH (44.8 mmol, 4 eq) was slowly added at 0° C. Reaction was cooled to room temperature and allowed to run overnight. Reaction was then quenched with acetone at 0° C and diluted with ether. 2.20 mL of water was added followed by the addition of 2.20 mL of 15% aqueous NaOH followed by the addition of 6.6 mL of water. Reaction was cooled to room temperature and stirred for 15 minutes. Anhydrous MgSO4 was added and after stirring for another 15 minutes the reaction was filtered and filtrate was concentrated to give pure ((9R,10R,12S)-9,10-dihydro-9,10-ethanoanthracene-11,12-diyl) dimethanol as a white powder.5

Synthesis of ((1'R,2'R,3'S,4'S)-1',2',3',4'-tetrahydro-[1,1':4',1"-terphenyl]-2',3'-diyl) dimethanol

Equimolar amounts of maleic anhydride (24.237 mmol) and trans,trans-1,4-diphenyl-1,3-butadiene were refluxed in p-xylene under nitrogen for 46 hours. Once cooled a white solid formed and was filtered, washed with either, and air dried. Further recrystallization from chloroform (350mL) yielded 3,6-diphenyl-cis-1,2,3,6tetrahydrophthalic anhydride (18.16 mmol, 5.53 g)⁶. Product was then dissolved in ether and DIBAL-H in hexanes (91.86 mmol, 5 eq) was carefully added at 0° C and stirred overnight. Reaction was quenched with aqueous HCL (1 M, ~100mL), then diluted with ethyl acetate and Rochelle salt was added and allowed to stir for 30 mins, then extracted with ethyl acetate (200×3) , then washed with brine and dried over MgSO₄. Further purification by silica gel column chromatography $(CH_2Cl_2/acetone=4/1)$ to give the pure product⁷.

Chemical Oxidation



Scheme 1

In order to make sure we were able to obtain a yield we first ran the reaction with our model substrate ((4,S,S,R)-2,2-dibenzyl-1,3-dioxolane-4,5-diyl) dimethanol via chemical oxidation with racemic catalyst ACT (*Scheme 1*). This showed proof of principle and verified that a lactonization at -40° C is obtainable. Once we obtained 70% yield with our racemic catalyst, we began looking at our chiral catalysts (*Figure 1*).



Figure 1: Chiral catalysts

When we performed the chemical oxidation with our chiral catalysts, we found that catalyst SR-II-013 and SR-I-224 had the highest enantiomeric excess and the highest yields *(Figure 2).* This is a trend that we continued to see in future experiments. Based on these results, we hypothesized that there is hydrogen bonding of the terminal N-H position. This was our first possible structure- reactivity relationship.

catalyst	%ee	%yield
SR-I-224	74	100
SR-II-012	20	98
SR-II-013	88	97
SR-II-014	49	102

Figure 2: Yield and %ee results from HPLC

The next substrate we looked at was ((9R,10R,12S)-9,10-dihydro-9,10ethanoanthracene-11,12-diyl) dimethanol *(Scheme 3)*. We ultimately saw low reactivity as well as low %ee. Even after 96 hours we were only able to isolate 40% yield. This could be because the substrate was insoluble in solution. This leads us to believe that solubility is key in achieving high reactivity. This catalyst may rely on hydrogen bonding to the backbone of the substrate. This substrate is sterically hindered and does not have any hydrogen accepting sites. SR-II-013 and SR-I-224 gave the highest %ee, although still relatively low (*Figure 3*).



Scheme 3: Catalysts: SR-I-224, SR-II-012, SR-II-013, SR-II-014

	96 h (quenched with EtOH)	96 h (8 h r.t.)
SR-1-224	12% ee†	8% ee [‡]
SR-II-012	6% ee†	$10\% ee^{\ddagger}$
SR-II-013	13% ee†	18% ee [*] *
SR-II-014	9% ee†	9% ee [‡]

[†] SM and HA [‡] full clean conversion (UPLC and GC-MS) *40% isolated yield *Figure 3: %ee results from HPLC*

By developing a method on the HPLC, we can quantify, isolate, and verify each product in the reaction (*Figure 4*).



Figure 4: Separation analysis developed on HPLC

The next substrate we choses to look at was(4R,5S)-1,3-dibenzyl-4,5bis(hydroxymethyl)imidazolidin-2-one (*Scheme 4*). This substrate's backbone has a similar structure to our lead substrate. Results showed low enantiomeric excess. Notably, the transformation using SR-II-013 delivered a 58%ee at around 50% conversion. The enantiomeric excess dropped off to 3%ee at 100% conversion (*Figure 5*). This conversion dependent %ee is indicative of a kinetic resolution of the hemiketal intermediate. Optimization of catalyst reactivity site may be needed.



Scheme 4: Catalysts SR-I-224, SR-II-012, SR-II-013, SR-II-014

	%ee	%yield (¹ H qNMR)	conversio	n
SR-I-224	12	57	100	
SR-II-012	3	69	100	
SR-II-013	3	68	100	42% isolated yield
SR-II-014	14	68	100	

Figure 5: Resulting %ee from HPLC and yield from ¹H qNMR

Electrochemical Oxidation

There are many factors that can affect the enantiomeric excess of a reaction: base, electrolyte, solvent, current, charge, sacrificial oxidant, electrode, catalyst loading, and concentration. If we were to test every condition it would come out to 230,947,200 experiments. For this reason, we utilized high-throughput microscale electrochemical (HTe⁻) screening techniques.⁸ By employing this method, we were able to run 24 different reactions at once, with the specific conditions we were interested in screening.

Plate Setup

Each cell was loaded with substrate, base, electrolyte, solvent, catalyst, and sacrificial oxidant in varying amounts depending on reaction conditions of the plate. All plates were run with carbon electrodes at -40° C in an insulated box with slight nitrogen flow to prevent condensation on the plate. Current and charge were then applied, and the reactions were allowed to run.



Scheme 5: Screening Bases

	^t BuCO ₂ Na	LIOTFE	NaOHFIP	Lutidine	TEA	DBU	
4 F	0	0	0	64	HA	HA	06-04
6 F	0	0	0	> 100	HA	HA	0.6 mA
4 F	0	0	0	81	HA	HA	0.2 mA
6 F	0	0	0	> 100	HA	HA	0.3 mA
	HA = Hemia	cetal					

Figure 6: %yield from HPLC

Before screening with the chiral catalysts, we ran the reaction using the racemic catalyst AZADO-ester (*Scheme 5*). Base is known to speed up the rate of alcohol oxidation.⁹ Initially at -40° C, we found high yield with 2,6-Lutedine as our base (*Figure 6*). When we tried to apply our conditions to our chiral catalysts, we saw a low %ee.



Scheme 6: Screening Catalyst, Base, Electrolyte

We decided to perform control experiments in order to determine what happened when we switched to the chiral catalysts (*Scheme 6*). These revealed that addition of electrolyte has a negligible effect on

enantiomeric excess and yield while 2,6-Lutidine has a deleterious effect (*Figure 7*).

	Sample	%ee	%yield
	SR-II-013	88	97
	SR-II-013 TEABF ₄	90	96
	SR-II-013 2,6- Lutidine	50	>99
=			

Figure 7: %ee and %yield from HPLC

An extensive screening campaign to find alternative bases revealed that cesium carbonate was effective at delivering the desired lactone when the current was lowered to 0.1 mA. The best condition gave a 70% yield and 68%ee. This provided good proof of principle for successful adoption of chemical conditions to the electrochemical pathway.

Conclusion

Ongoing efforts for catalyst optimization will hopefully increase the resulting enantiomeric excess. We believe the catalyst reacts at the terminal N-H position; thus, we will continue to adjust substitution on the proposed reactivity site.⁹ Chemical lactonization screening of all future substrates with optimal conditions and best optimized catalysts will take place. Once significant yields and %ee are observed the same reactions will occur electrochemically. Once our method is developed future optimization of our catalysts will allow for efficient synthesis of precursors in industry.

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ABBREVIATIONS

HPLC, high performance liquid chromatography; HTE, high-throughput experimentation;

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The Crossover Between Batteries and Supercapacitors in Metal Sulfide Nanoparticles

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Abstract

The high-power density, long cyclability, and high energy performance of supercapacitors (SC) have increased the attention of many researchers. When metal sulfides are used as the main component of SC's, the ion transport is known as pseudocapacitance, which follows the Faradaic reaction principle. SC's have the ability to improve energy efficiency, power, and flexibility, making them a promising renewable energy source. This research presents the possibility of electrophoretic deposition (EPD) as a powerful technique to deposit charged nanoparticles onto a specific substrate. The employment of the EPD technique can help increase the porosity of the deposited film, therefore increasing the energy density of SC's. This report will describe how copper sulfide (Cu_2S) nanoparticles can be deposited when EPD is used. Also, results obtained by varying the voltages, deposition time, and nanoparticle concentration during EPD will be shown.

Introduction

The development of novel renewable energystorage devices is crucial due to the current high usage of non-renewable energy and its impact on climate change¹. The commercialization of lithium-ion batteries by Sony opened up new avenues in energy research. In recent years, it has been found that changing the size of the particles used during lithium-ion battery assembly can lead to new technologies and applications. Moreover, nanoparticles can be used to modify supercapacitors' properties. For example, the use of nanoparticles can increase the chance of enhancing energy and power density, thus increasing their efficacy and market value². Yus studied how the high surface area of nanoparticles will extend the life, performance, cyclability, and resistance of SC's¹.

Since the discovery of the battery in 1800 by Volta, the global increase in energy demand has driven the scientific community to improve battery performance ³. Batteries oxidation-reduction follow an (redox) reaction. During redox reactions, oxidation occurs at the anode, while reduction occurs at the cathode. These redox reactions make the battery have a high energy density but slow kinetics⁴. As in batteries, when metal oxide or metal sulfide nanoparticles are used in supercapacitors, the mechanism followed is electrochemical pseudocapacitance storage of charge, which is a very fast reversible 5 reaction As faradaic a result. pseudocapacitors typically contain a higher energy density than batteries and electric double-layer capacitors ⁶. . Researchers have found that sulfide copper (Cu_2S) nanoparticles are able to increase the energy density of SC due to their high capacitance⁷.

Thus, copper sulfide nanoparticles were used in this research.

Critical Parameters	Capacitors	Supercapacitors	Batteries
Energy density (Wh/kg) Power density (W/kg) Time of charge (s) Time of discharge (s) Cyclability Typical lifetime (years) Efficiency (%)	0.1 10 ⁷	3-10 3000 0.3-30 0.3-30 10 ⁶ 30 85-08	100 100 >1000 1000-10,000 1000 5 70-85

Figure 1. Differences between critical parameters of batteries, capacitors, and supercapacitors.⁴

As can be seen in **Figure 1**, supercapacitors have a very high power density, which means they can deliver energy much faster than a battery can. However, supercapacitors have a low energy density. This issue can be addressed by using the method of electrophoretic deposition to deposit Cu_2S nanoparticles onto the substrate, which can increase the capacitance and porosity of the energy device.

Electrophoretic deposition is a technique developed by G.M Bose around 1880, and its application started in the late 1900s⁸. Colloidal processes such as EPD make possible the adhesion of different materials. covering complex tridimensional surfaces and creating a homogenous film. Using this method, the thickness and morphology of the deposited film can be controlled by changing the voltage, time of deposition, solution concentration, and distance between electrodes. The versatility and costeffectiveness of this technique makes it attractive for practical uses. For example, EPD can be used to deposit proteins, enzymes, and biopolymers for biomedical devices: it also can be used for ceramic composites and micro/nanoscale particles for 9–11 applications sustainable energy Parameters which can affect the density of the deposited film are the zeta potential, deposition time. applied voltage. conductivity of the substrate. and concentration of the nanoparticles in suspension ¹². This study will report how the

porosity percentage along the film can be affected when applying different voltages. Also, the importance of solution concentration on deposition will be discussed, as well as the effect of increasing voltage on the thickness of the deposited film.

Materials

All materials were analytically pure and did not require further purification.

Cu₂S nanoparticles (previously synthesized), toluene (Sigma Aldrich, 99%), oleylamine (Sigma Aldrich, 70%), sonicator, Regulated Kepco DC supply (0 - 1.5 kV), stainless steel electrodes.

Experimental

Copper Sulfide (Cu₂S) Nanoparticles

The copper sulfide (Cu₂S) nanoparticles used in the experiments were previously synthesized in 2015 by a previous member of the research group.

Electrophoretic Deposition (EPD)

For all EPD trials, the nanoparticle deposited was Cu_2S , and the solvent used was toluene.

The applied voltage and deposition time were varied across trials to verify the difference in packing density on the copper plate and its effect on deposition and electrostatic potential between the electrodes. Furthermore, it was investigated whether using a new solution for each trial or reusing the same solution for multiple trials had any effects on deposited mass.

EPD was done using a Regulated Kepco DC power supply and stainless-steel electrodes. A new setup was designed to improve the reproducibility of the experiments. This new setup also allowed for variations in distance between electrodes; it was difficult to consistently vary distances using the old setup.



Figure 2. Setup used for EPD experiments

To reduce the particle size and reduce agglomeration of particles, the Cu₂S nanoparticles were grinded using a mortar and pestle. Then, 120 mg of the crushed nanoparticles were added into a beaker containing 1 mL of oleylamine. The solution was stirred at 80°C or one hour to increase the colloidal stability of the nanoparticle by attaching ligands to its surface. After this, 45 mL of toluene was added, and the resulting solution was sonicated (with heat) for one hour.

Approximately 15 mL of the total 45 mL of solution was poured into a 20 mL beaker. The mass of a clean copper plate was measured, and the plate was stuck onto the positive electrode using double-sided tape. The electrodes were then placed into the 20 mL beaker, and the wires from the power source were connected to the electrodes.

For the first set of deposition trials, the voltage was varied from 150 V to 900 V (in increments of 150V), while holding the deposition time (10 mins) and distance between electrodes (2 mm) constant. The next set of trials was carried out in the same way as the first set, with the exception that the deposition time was now held constant at 15 mins. For these first two sets of trials, after each trial, the 15 mL of solution in the beaker was placed back into the centrifuge tube containing the other 30 mL of solution. This centrifuge tube was shaken by hand to mix

the solution, and 15 mL of this "recycled" solution was poured into the beaker to be used for the next trial.

The third and fourth sets of deposition trials were carried out by using the same parameters as the first and second set of trials, respectively, with the exception that for each trial, the 15 mL of solution used was discarded instead of being mixed back with the other 30 mL of solution and "recycled."

After each EPD trial, the copper plate was removed from the electrode, and any tape and tape residue which remained on the back of the plate was cleaned off using hexane. This hexane, as well as the toluene from the solution, was allowed to evaporate from the plate. The mass of the copper plate was then measured. The change in mass of the plate before and after deposition was calculated to find the mass deposited onto the copper plate.

Results and Discussion

In general, a solution containing copper sulfide nanoparticles negatively charge by oleylamine (ligand) in its surface and dissolved in Toluene was used for each of the experiments. For the trials whose data is shown in **Table 1**, "recycled" solution was used. As can be seen, the deposited mass does not follow any trend in terms of deposited mass.

Voltage	10 min.	15 min.
150 V	+2.03 mg	+1.42 mg
300 V	+1.47 mg	+0.66 mg
450 V	+3.90 mg	+0.89 mg
600V	+4.59 mg	+1.32 mg
750 V	+1.36 mg	+0.66 mg
900 V	+2.24 mg	+0.58 mg
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 Table 1. Voltage Vs. Time: Recycled solution used

To further investigate whether recycling the solution affects the deposited mass, three trials were carried out in succession by holding time and voltage constant but recycling the solution between each trial.



Since these three trials under the same voltage and time conditions showed a decrease in deposited mass as the solution was recycled between each trial, it can be seen that recycling the solution affected the deposited mass.

Voltage	10 min.	15 min.
150 V	+2.33 mg	+1.15 mg
300 V	+2.97 mg	+2.79 mg
450 V	+1.98 mg	+1.87 mg
600V	+5.33 mg	+2.60 mg
750 V	+5.31 mg	+2.32 mg
900 V	+6.37 mg	+5.00 mg

Table 2. Voltage Vs. Time: New solution used

After this finding, a new solution for each trial was used to prevent changes in concentration. **Tables 1 and 2** show that in nearly every case, when a fresh solution was used, the deposited mass was higher as compared to when the solution was recycled. Also, when a new solution is used for each trial and the voltage is increased, a higher mass is obtained.

Additionally, the fresh solution trials yielded thicker films as compared to the recycled solution trials. The Keyence VK-X260 Laser-Scanning Confocal Microscope (LSCM) was used to measure and observe the thickness of the deposited film. Before observing the film in the LSCM, some of the deposition on the copper plate was removed

using hexane, exposing the clean plate. This was done so that the difference in height between the clean copper plate and the deposited film can be seen in the LSCM. When first analyzing the sample, a photo of the entire copper plate was taken at a magnification of 10X. The magnification was then changed to 150X, and a range of 25-30 images were taken for each sample. The Keyence MultiFile Analyzer software was used to find the experimental thickness of the film. Table 3-4 demonstrates the significant impact the solution of concentration on the film thickness; it can be seen that when a new solution is used for each trial, the thickness of the film does not vary as much as when the solution is recycled between each of the six trials. It is essential to clarify that the trials with the recycled solution were done in random order to eliminate the possibility of seeing a decrease in deposited mass when increasing voltage due to lost concentration.

Voltage	10 min.	15 min.
150 V	2.03 µm	7.02 μm
300 V	1.47 μm	2.11 μm
450 V	3.9 µm	0.94 µm
600V	4.59 μm	2.84 µm
750 V	1.36 µm	0.91 µm
900 V	2.24 µm	1.51 μm

 Table 3. Experimental Thickness: inconsistent concentration used

Voltage	10 min.	15 min.
150 V	2.33 µm	3.00 µт
300 V	2.97 µm	7.57 μm
450 V	1.98 µm	5.21 µm
600V	5.33 µm	5.46 µm
750 V	5.31 µm	5.96 µm
900 V	6.37 μm	8.44 μm

 Table 4. Experimental Thickness: Consistent concentration used

Increasing the voltage increases the appearance of a cracking pattern in the film, despite the increase **Table 4**, in the trial done for 15 minutes at 900 V, the experimental thickness of the film could not be calculated due to a significant amount of cracking on the plate.



Diagram 2. Difference in deposition uniformity between lowest and highest voltages

After finishing the trials, it has been seen that the uniformity of the films decreases when increasing the voltage. The latter can directly affect the calculated porosity since the is very sensitive to changes in heights



Graph 1: Samples' experimental thickness with its standard deviation

The data used to develop Graph 1 was obtained from Table 4. To verify the uniformity of the experimental thickness for each of the samples, a standard deviation was The calculation calculated. was done considering the different measured thicknesses using the LSCM. As shown in the graph, the thickness of the 10 minute trials with a fresh solution increases with the voltage and also, its standard deviation increases as well. This means that thickness uniformity is reduced at high voltages. Since the thickness of the 15 minute sample film remains more uniform and the standard deviation does not increase, it appears to have the best uniformity.



data

The equation to calculate the theoretical height (h) for each sample was: $h = \frac{m}{d r^2 \pi}$. In this equation, m is the deposited mass, d is the density of the Copper Sulfide nanoparticles, and r the radius of the Copper plate used as a substrate. After acquiring these values, the theoretical height (h) was calculated for each of the samples. To calculate the porosity, the following equation was used: *porosity* = $\frac{experimental height-theoretical height}{experimental height}$. The

experimental height, previously calculated using LSCM showed in **Table 4**, was used to develop **Graph 2**. Also, for **Graph 2** a standard deviation was calculated to verify the porosity variation between films. As seen in the graph, porosity was acquired for each film but with high standard deviation numbers. The latter demonstrates that no uniform porosity was acquired.

Conclusion

In conclusion, when the EPD technique is used, porosity can be acquired. In terms of future work, more trials should be done to verify the reproducibility of each trial. Additionally, changes in distance between electrodes and different substrate materials should be tested to verify differences in experimental.

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Robust Methodology for Third Harmonic Generation Using Quasi-Phase Matching

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Despite the ubiquity of nth-harmonic generation in wave-mixing, there remains a fundamental concern with achieving high efficiencies using Third-Harmonic Generation (THG) in three-wave mixing scenarios for broadband applications. We investigate a specific system rising from four different photon interactions associated with Sum-Frequency-Generation (SFG), and nth-harmonic generation, that gives rise to exotic, harnessable dynamics. Particulary, we investigate a system with projected utility in use with broadband pulses, where one of it's four photon interactions is snuffed out by means of lacking in phase-matching, and where the remaining processes are matched artificially by the use of Quasi-Phase Matching (QPM).

I. INTRODUCTION

Wave-mixing processes in nonlinear, optical media are commonplace for characterization¹, or the output of lesser-seen frequencies at particular intensities. These processes are heavily reliant, and dominated in the length of their propagation by the second-order nonlinear susceptibility $\chi^{(2)}$ of the in-situ material associated with the process. However, the limitations on these processes can be very clear-cut. Oscillatory behavior is very common in three-wave-mixing (Fig. 1a), with a particular exception in Second-Harmonic generation (Fig. 1b), where one sees convergent behavior for corresponding amplitudes.

In general, the dynamics of each wave-mixing process can be described by a set of nonlinear, coupled ODE's. Take SHG, a process that is often used for efficient gen-



(a) Optical Parametric Amplification (OPA)



FIG. 1: Intensity for each wave vs. ζ for two nonlinear wave-mixing processes. Perfect phase-matching case.

eration of the second-harmonic of an input frequency ω_1 . We can describe the dynamics of a 1-dimensional SHG process (Fig. 2) as follows²:

$$\frac{dA_1}{dz} = \frac{2id_{eff}\omega_1^2}{k_1c^2}A_3A_2^*e^{-i\Delta kz}$$
$$\frac{dA_2}{dz} = \frac{id_{eff}\omega_2^2}{k_2c^2}A_1^2e^{i\Delta kz}$$

Where the exponential term on each equation depends on the phase-matching of the respective waves:

$$\Delta k = k_2 - 2k_1$$

And where we define A_i , ω_i as the amplitude and frequency of the respective wave, $d_{eff} = \frac{\chi_2}{2}$, and z as the propagation distance in the axis of interest.

We define a process, or combination of processes as perfectly phase-matched when all Δk values are 0. A lack of perfect phase-matching will cause a lack of full conversion in some processes, and back-conversion in others; generally being an unwanted condition. However, achieving perfect phase-matching is only possible in birefringent materials, and at times is even impossible for more complicated, hybrid processes.

In the case of a phase-mismatch, there are many methods of QPM that can be utilized to artificially match processes substantially, if not completely. We will utilize the method of QPM defined in *Norton and Sterke*³, where the polarization of a material is changed many times to make the value of d_{eff} a function of distance. We define this new value of d_{eff} :

$$d_{eff} = d_{eff}(0)sign[\sum_{i} \alpha_{i}sin(\Delta k_{i}z)]$$
(1)



FIG. 2: Input and output waves for SHG².

The resulting function is a periodic square wave with only one phase-mismatch, and an aperiodic wave with multiple mismatches (e.g, Fig. 4b). α values can be changed to weigh specific processes. This methodology does not always replicate results of perfect phasematching exactly, often resulting in an increase in propagation distance for similar dynamics, or back-conversion. Regardless, QPM provides a useful alternative to the use of birefringent crystals, and can be used creatively to manipulate the value of d_{eff} .

In succeeding sections, we investigate the utility of hybrid three-wave-mixing processes as seen in recent works. A less-seen system of hybrid processes will be investigated using similar fundamentals, to search for interesting dynamics. An argument will be made for a different method of THG with the aforementioned system that could yield higher efficiencies with broadband pulse inputs, and simulations with realistic parameters and materials will be investigated.

II. HYBRID PROCESSES

There are multiple objectives associated with wavemixing processes. A well-know example is OPA, by which one may amplify an input signal wave's intensity with an input pump wave. This process' efficiency is detrimented by the periodic nature of associated dynamics (see Fig. 1a), and how these dynamics affect realistic



FIG. 3: Two different QPM structures. (a) Snapshot of periodic QPM in a Lithium Niobate Crystal⁴. (b) Aperiodic structure for Sum-/Difference-frequency generation as seen in $Moses, et.al^5$.

input pulses. Gaussian spatiotemporal profiles can limit conversion down to 15-30% in OPA^5 . As such, an investigation on how to optimize these processes is always of interest, and one of the primary ways to pursue higher efficiencies is to seek new exotic systems that may appeal to the spatiotemporal nature of pulses.

A. Second-Harmonic Amplification (SHA)

 $Flemens^6$ depicts a hybrid OPA with simultaneous SHG system (Fig 4c). Long-term dynamics are convergent in nature, and achieve up to 55% efficiency with broadband pulses.



FIG. 4: Fractional photon flux vs. distance ζ for 3 perfectly phase-matched processes. Regular OPA process followed by QPA; a method similar to OPA with additional displacement of idler photons to their second harmonic. Final graph depicts SHA, a process with convergent behavior for output waves, and with markedly higher efficiency for broadband pulses.

We describe the system through a set of coupled ODE's:

$$\begin{aligned} \frac{dA_s}{dz} &= \frac{i\omega_s d_{eff}}{n_s c} A_p A_i^* e^{i\Delta k_{OPA}z} \\ \frac{dA_p}{dz} &= \frac{i\omega_p d_{eff}}{n_p c} A_s A_i e^{-i\Delta k_{OPA}z} \\ \frac{dA_i}{dz} &= \frac{i\omega_i}{n_i c} [d_{eff} A_p A_s^* e^{i\Delta k_{OPA}z} + d_{effs} A_{2i} A_i^* e^{i\Delta k_{SHG}z}] \\ \frac{dA_{2i}}{dz} &= \frac{i\omega_{2i} d_{eff}}{2n_{2i} c} A_i^2 e^{-i\Delta k_{SHG}z} \end{aligned}$$

With signal, pump, idler, and idler second-harmonic frequencies respectively, and with phase mismatches

 $\Delta k_{OPA} = k_p - k_s - k_i$, and $\Delta k_{SHG} = k_{2i} - 2k_i$. It is important to note that the d_{eff} term in the prior equation can differ between the two different processes given the use of QPM.

Analytical solutions in the perfectly phase-matched scenario depict a behaviorally equivalent solution to a damped Duffing oscillator for each wave. The most interesting parameter for analysis is the damping ratio:

$$\gamma(\zeta) = iU_{2i}\sqrt{\frac{n_s n_p \omega_i \omega_{2i}}{n_i n_{2i} \omega_s \omega_p}} \frac{d_{eff_S}}{d_{eff_o}} \tag{2}$$

With $A_k = U_k \sqrt{\frac{\hbar\omega_k F_0}{2n_k \epsilon_0}}$, a convention that will also be used in later analysis.



FIG. 5: Photon interactions for the 211 - 321 - 422 - 431 System.

The fraction $\frac{d_{effs}}{d_{effo}}$ is proportional to the weighting of ratios of χ_2 for SHG vs. OPA; a quantity that is only mutable with the use of QPM by changing α values in eq. 1. Exact behavior in eq. 2 can be hard to predict quantitatively, but one can generalize the long term behavior by $\gamma(\infty) = \|U_{p,0}\|^2 \sqrt{\frac{n_s n_p \omega_i \omega_{2i}}{n_i n_{2i} \omega_s \omega_p}} \frac{d_{effs}}{d_{effo}}$. This value is fully calculable, with the dynamics of an under-damped oscillator when $\gamma(\infty) < 1$, over-damped when $\gamma(\infty) > 1$, and critical damping when $\gamma(\infty) = 1$.

Damped oscillator behavior proves to be a desirable and realistic outcome for convergent solutions, and similar behavior will be seen and described in a later structure to provide a case for efficient THG.

B. 211 - 321 - 422 - 431 System

Commonly explored three-wave-mixing processes include Fourth-Harmonic generation, and Third-Harmonic generation (most commonly through SFG, or hybrid SHG + SFG)⁷. The primary system of interest in this paper involves four different processes. SHG (fig 5a(i)), and FHG (fig 5a(ii)) processes are generally unidirectional, and an argument can be made through analysis of eigenmodes for further clarity on directionality for remaining processes (although this is out of the scope of this paper). For our analysis, we assume input waves are continuous, single-frequency waves.

We utilize a simple convention for differentiating each process; where the first digit of the process is the output wave from either harmonic-generation or SFG, and the remaining two digits are multiples of the fundamental frequency added in the process. E.g: process 321 represents the $\omega_3 = 3\omega_1 = 2\omega_1 + 1\omega_1$ photon interaction. We represent this hybrid system through a set of coupled ODE's:

$$\begin{cases} \frac{dA_1}{dz} = i\kappa_1 (A_2\bar{A}_1 e^{i\Delta k_{211}z} + A_3\bar{A}_2 e^{i\Delta k_{321}z} + A_4\bar{A}_3 e^{i\Delta k_{431}z}) \\ \frac{dA_2}{dz} = i\kappa_2 (\frac{1}{2}A_1^2 e^{-i\Delta k_{211}z} + A_3\bar{A}_1 e^{i\Delta k_{321}z} + A_4\bar{A}_2 e^{i\Delta k_{422}z}) \\ \frac{dA_3}{dz} = i\kappa_3 (A_2A_1 e^{-i\Delta k_{321}z} + A_4\bar{A}_1 e^{i\Delta k_{431}z}) \\ \frac{dA_4}{dz} = i\kappa_4 (\frac{1}{2}A_2^2 e^{-i\Delta k_{422}z} + A_3A_1 e^{-i\Delta k_{431}z}) \end{cases}$$

For simplicity of analysis, we let the system be perfectly phase-matched with regards to every process. Furthermore, substitutions are made to non-dimensionalize relevant equations:

$$\begin{cases} \frac{dU_1}{dz} = i(2\Gamma_{211}U_2U_1^* + \Gamma_{321}U_3U_2^* + \Gamma_{431}U_4U_3^*) \\ \frac{dU_2}{dz} = i(\Gamma_{211}U_1^2 + \Gamma_{321}U_3U_1^* + 2\Gamma_{422}U_4U_2^*) \\ \frac{dU_3}{dz} = i(\Gamma_{321}U_2U_1 + \Gamma_{431}U_4U_1^*) \\ \frac{dU_4}{dz} = i(\Gamma_{422}U_2^2 + \Gamma_{431}U_3U_1) \end{cases}$$
(3)

 Γ values in eq. 3 serve to weigh each process. Characteristic dynamics are defined by the weightings of each process with regards to others, while the observation can be made that increasing the magnitude of all processes simultaneously will reduce propagation distance required for the defining behaviors of each scenario.



FIG. 6: Various permutations of Γ ratios for 211 - 321 -422 - 431 system. a) All Γ values are equal. Natural convergence to the same fractional photon flux for all waves. b) 422 process weighted less than remaining processes. Complicated oscillatory behavior that eventually converges. c) 321 and 431 process weighted higher than remaining processes. Starts with mild

oscillations, eventually converting to a fully periodic system. d) 321 weighted less than remaining processes. Third Harmonic converges with high efficiency. Figure 6 serves to illustrate unique behaviors that can occur with different weights for each process. Useful behaviors tends to manifest in systems with convergent dynamics and high theoretical efficiencies for conversion. Something to particularly avoid is back-conversion in a system (i.e, periodic behaviors).

Of particular interest is fig. 6d. Third-Harmonic generation is known to be a relatively inefficient process for broadband-waves, at typically a few percent with threewave-mixing. Weighing the 321 process weakly (what regularly is considered the THG process) appears to increase the peak flux of the Third-Harmonic wave, in addition to resulting in convergent long-term behavior. As such, the pursuit of a realistic experimental application of these conditions is attractive to optimizing the generation of Third-Harmonic frequencies.

III. UTILIZING QPM TO OUTPUT EFFICIENT THG

It is relatively simple to deter a specific process in a hybrid system (in this case, our 321 interaction), by assuring that it progresses with a substantial phase mismatch. We will simply refer to this new 211 - 422 - 431 process - where the 321 process is snuffed out - as "novel THG." Relevant equations for this system are shown:

$$\begin{cases} \frac{dU_1}{dz} = i(2\Gamma_{211}U_2U_1^* + \Gamma_{431}U_4U_3^*) \\ \frac{dU_2}{dz} = i(\Gamma_{211}U_1^2 + 2\Gamma_{422}U_4U_2^*) \\ \frac{dU_3}{dz} = i(\Gamma_{431}U_4U_1^*) \\ \frac{dU_4}{dz} = i(\Gamma_{422}U_2^2 + \Gamma_{431}U_3U_1) \end{cases}$$

$$\tag{4}$$

The flow of conversion for this system is shown in figure 7. The unintuitive result is then that the most efficient, convergent solutions for the Third-Harmonic are a result of back-conversion from the Fourth-Harmonic. We can analyse system dynamics by applying the same treatment as SHA in section II (A). We compare the system to a duffing oscillator, and through a few operations, one obtains an expression for the damping constant of the system:

$$\gamma(\zeta) = i \frac{\sqrt{3}}{3} \left(\frac{\sqrt{2}d_{211}U_2^*}{2d_{431}} \sqrt{\frac{n_3 n_4}{n_1 n_2}} + \frac{d_{422}U_2^2}{d_{431}U_4} \sqrt{\frac{n_1 n_3}{n_2^2}} \right) \quad (5)$$

Where U_2 , $U_4 \in i\mathbb{R} \forall \zeta$; i.e, $\gamma(\zeta) \in \mathbb{R} \forall \zeta$. The value of γ can be a bit uncertain. In general, it is the case that both terms in eq. 5 are positive. U_2 tends to be fully positive/imaginary, and U_4 tend to be fully negative/imaginary for all ζ , but succinct eigenmode analysis has yet to be done to observe different behavior, or objectively characterize the system.

A simulation to solve eq. 4 is ran. Specifically, we simulate this system under a LiNbO₃ crystal⁸, with $2\mu m$ light, and differing values of intensities (in general, 0.1 GW/cm²). Even in birefringent crystals, it is extremely difficult, if even possible, to manufacture a scenario where



FIG. 7: Flow of conversion for a new 211 - 422 - 431 process. Full conversion from the fundamental frequency to the Second-Harmonic through SHG, and to the Fourth-Harmonic with cascaded FHG.
Fourth-Harmonic tends to back-convert to the Third-Harmonic where it converges, and back to the fundamental where the photon processes repeat.

there is three different perfect phase-matchings. Instead, we turn to QPM to provide for a structure to cancel out exponential terms in eq. 4. We utilize eq. 1 to provide for a new value of d_{eff} . A term for Δk_{321} is explicitly not included to leave the phase-matching condition for that process unfulfilled. Figure 8 depicts the first few domains of the QPM grating for the simulation.



FIG. 8: First few domains of QPM structure for LiNbO₃ crystal, with $I = 0.1 GW/cm^2$. Manufacturing restrictions not applied.

QPM becomes an inapt method to achieve phasematched results when $\Lambda = \frac{2\pi}{\Delta k_i} \sim \Gamma_i$. QPM terms then become akin to a laser detuning term for the system, and can lead to noisy, and inaccurate dynamics. An example is illustrated in fig. 9.



FIG. 9: Novel THG with KTP crystal; $10GW/cm^2$. Dynamics occur on a similar scale as QPM detuning leading to noisy and inaccurate replication of novel THG (fig. 6d).



FIG. 10: Graphs of fractional photon flux vs. distance z (mm) through LNB crystal, using a $2\mu m$ wave. $I = 0.1 GW/cm^2$

In general, back-conversion due to QPM can be delayed further by increasing the magnitude of phasemismatches, or by decreasing Γ values (increasing propagation distance for dynamics). As a result, choosing the right intensity for this procedure is important to achieve a proper Quasi-Phase-Matched system (in this case, $\Gamma \propto \sqrt{I}$). Results of the simulation are pictured in figure 10, along with regular THG using the same system parameters. Long-term, convergent behavior similar to

5

fig. 6d is achieved until a point of back-conversion due to phase-matching with QPM. Ideally, one may cut the crystal near 1 cm to harness useful dynamics before backconversion (though this may change the QPM structure slightly). It is important to note that changing Γ values even a substantial amount does nothing to change longterm behavior, and simply seems to change damping in the system - thus making this a system robust to changes in parameter.

IV. DISCUSSION AND OUTLOOK

A novel method of THG (211 - 422 - 431) has been investigated and appears to provide for short-term convergent behavior superior to regular THG (211 - 321) methods for converting broadband pulses. Inhomogeneity in cycle period can be abated by dynamics found in this robust method of THG; limiting the effects of uneven spatiotemporal conversion - even in the non-ideal case where QPM is required.

QPM structures can assist in making similar systems realizable in an experimental setting. Figure 8 has domains with substantial variance, but mostly going over minimum domain size requirements (1-2 μm for most applications). Specifically, aperiodic poling is physically achievable even with multiple phase-mismatches given proper rounding methodology. There is a clear trade-off between perfect phase-matching, and the use of QPM, but the latter provides an inexpensive and noncomplicated way of replicating ideal behavior to a satisfying degree.

Further investigation is to be done. Specifically, eigenmode analysis for the 211 - 422 - 431 system has been neglected, and broadband pulse simulations have yet to be done. However, through representative simulations, an argument can be made for harnessing the useful dynamics present in this system, and future analysis with pulsed inputs appears to be a promising endeavor for efficient generation of Third-Harmonic frequencies with three-wave-mixing processes.

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Simulating approximate quantum operator dynamics using cellular automata

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A 1+1D cellular automaton model in the infinite temperature limit is constructed to study universal dynamics of operator spreading in quantum many-body systems, and to derive global equations of operator spreading behavior in the long-distance late-time limit. Stochastic parameters in the model are fixed periodically in time, imitating a Floquet Hamiltonian to introduce time-translational periodicity to automaton evolution rules. We consider various regimes of the stochastic parameters and Floquet period for effectively infinite system size. Rare events such as a front velocity of 0 after a period-dependent timescale materialize in average runs at small Floquet periods, but are suppressed for larger Floquet periods. Universally, bulk periodicity occurs with a period equal to the driving Floquet period. Additionally, for low ranges of the stochastic parameters, front velocity decreases with decreasing Floquet period.

I. INTRODUCTION

Universal dynamics of quantum many-body systems and granular 'hydrodynamic' equations to describe these are an active area of research, and will aid future research on charge and energy transport in physical systems.[4][1]

In quantum operator evolution, a single operator can grow and spread in spacetime according to Heisenberg evolution rules, where we transform an operator in time as opposed to propagating a wavefunction or evolving a state. The Heisenberg evolution for an operator A is

$$A(t) = e^{\frac{iHt}{\hbar}} A(t=0) e^{\frac{-iHt}{\hbar}}$$

where the Hamiltonian H exhibits time-translational invariance. This evolution allows the operator to propagate.

Cellular automata (CA) are mathematical models of physical systems that are discrete in time and space and evolve according to a set of rules assigned to them. They are typically adopted as a computationally cheaper option to model a system that evolves in time according to first or second order differential equations. Some systems that have been successfully modeled by cellular automata include bacterial colony growth, parallel processors, and wildfire spread.[2][8][3]

Classical cellular automata are a dramatically simplified approximation for quantum operator spreading, as we cannot simulate the quantum effects of entanglement in classical configuration space. Quantum cellular automata, which preserve this aspect of quantum manybody systems, are an area of active research.[6][7] Therefore, we know that any universal dynamics we extract are not due to entanglement effects, coupling, and superpositions. Even without these features of real quantum systems, classical cellular automata can be useful tools for studying the behavior of quantum operator spreading due to their linear scaling with system size. One of the challenges of studying quantum systems is the exponential scaling of the Hilbert space with system size. This occurs because in order to fully specify the state of a qubit, two complex numbers are needed, so 2^N numbers are needed to fully specify the state of N qubits. This scaling sets computational bounds on models of quantum systems and causes finite system effects to quickly factor in these models. To specify the state of N classical bits, only N numbers are needed, as one number alone specifies a bit state. This enables us to scale classical models to effectively infinite system size, and greatly reduces computational complexity.

Working with a cellular automaton model, the goal of this study was to extract universal dynamics of the behavior of the system at long distances and late times. At late times, we expect transients to die out, so that any global behavior the system exhibits should be seen in this regime. The stochastic parameters in the CA evolution rules were applied periodically to simulate a Floquet Hamiltonian, which resulted in bulk periodicity with a period equal to the Floquet period, and perioddriven separation of front velocities for low ranges of the stochastic parameters.

II. MODEL

A. Review of Cellular Automaton Implementation

The cellular automaton can be visualized as a grid in spacetime, as this is a discrete configuration space. Physically, the operators occupying this space are the identity operator 1 and the three Pauli matrices σ_x , σ_y , and σ_z , which form a complete basis. Since the sites in this grid

in configuration space can take on only binary values 0 or 1, we let the 0 state be uniquely occupied by the identity operator, and the 1 state be any of the three Pauli operators. We start with a Pauli matrix at the origin in the first time step, and let this operator propagate or die at each time step with a certain probability according to the rules we have assigned.

The fixed rules assigned to the cellular automaton model were developed by Sridhar Prabhu and were designed to simulate operator spread with a linear combination of terms, including terms for operator continuation, propagation, collision, and termination.[5] The highly constrained regime of the more general rule that is explored here can be expressed as

$$\begin{split} C(r,t+1) &= C(r,t) + (1-C(r,t))H(I(r,t)) - \Gamma C(r,t) \\ I(r,t) &= \xi (C(r-1,t) + C(r+1,t)) \\ \xi &= \begin{cases} 1 & \text{with probability } p \\ 0 & \text{with probability } 1-p \end{cases} \end{split}$$

$$\Gamma = \begin{cases} 1 & \text{with probability } q \\ 0 & \text{with probability } 1 - q \end{cases}$$

Here, C(r, t) is the binary state of the bit and C(r, t+1)is the binary state of the bit at the next time update. The first term in the master rule allows for the default of the evolution to be steady-state. The second term is the propagation term, which factors for a site if the site was inactive (occupied by an identity operator) for the previous timestep. In this term, H(x) is the Heaviside function, and I(r,t) is the 'interaction', which is nonzero if the neighborhood of length one on either side of the cell is nonzero (contains a Pauli operator), or if the coupled sites, of which there are none in this constrained version, are nonzero. This term governs the upper limit on the rate of information spread in the system, called the Lieb-Robinson bound. The Lieb-Robinson velocity, v_{LR} , in this system is trivially 1, since the propagation neighborhood only extends to adjacent sites. The third term is the operator 'death' term; a Pauli operator can transform into the identity operator if its site was occupied by a Pauli operator in the most recent time step. This is a feature of the constrained model; in the general model, this operator 'lifetime' can be tuned by a parameter τ . The only surviving non-deterministic aspects of this constrained rule set are the stochastic parameters p and q, which determine the binary values of ξ and Γ , respectively. We hope to extract universal behaviors from this rule set by tuning these parameters and updating them on various timescales.

The cellular automaton was implemented in Python 2.7, and universal behavior was identified using a Monte Carlo simulation. Typically, data was obtained by averaging the values of C(r, t) over 100 runs so that any rare events would be suppressed by repeating runs, and only behavior common to all runs would survive in the averaged realization. The initial configuration for each run is a single Pauli operator at the central or 'origin' site in the single spatial dimension at the first time step;

$$C(r,0) = \begin{cases} 1 & r = origin \\ 0 & else \end{cases}$$

This operator then evolves according to the constrained rule set. This spreading creates the visual of a light cone for operators undergoing ballistic spread. After averaging over many runs, bulk and L/R front values can be defined at each time step in the light cone. Here, the value of the bulk is the average over the origin and 10 adjacent sites on either side. The value of the left and right fronts of the light cone are location of the maximum change in site values C(r, t) over the spatial locations; spatially this sits between the sites that the lightcone has not yet reached and the sites in the lightcone whose values are comparable to the bulk value. The front propagates outward with some velocity v_F , the front velocity. v_F is determined by the value in that run of the stochastic parameters. Since p is the growth parameter, tuning up p for fixed q will yield a higher front velocity and a broader lightcone. Conversely, increasing q, the death parameter, for fixed p will decrease front velocity, producing a narrower lightcone.

B. Stochastic Parameter Tuning

In the CA rules, every site has its own value of p and q. In the first version of this model, p and q were updated for every site at every timestep (this was done randomly, using the Python random() function in the random module). However, in a quantum system like the one we are simulating, we usually deal with Hamiltonians that are time-translationally invariant. Although these CA rules are not simulating Hamiltonian dynamics, I wanted to introduce some notion of time-translational invariance to the system. In order to do this, I introduced a parameter g, which specified the probability that p would update for every site for the next timestep. With this new parameter, it is possible to define a lifetime G for a realization of p, where

$$G = \frac{1}{g}.$$

The next version of my p, q update was periodic, in order to imitate a Floquet Hamiltonian, which is periodic in time such that for a Hamiltonian \hat{H} and a Floquet period T,

$$\hat{H}_{Floquet}(t) = \hat{H}_{Floquet}(t+T).$$

While the first update method was useful in determining which combinations of p and q produce a light cone, the results from the Floquet updates were the most interesting and succeeded in capturing some essence of timetranslational invariance in the CA rules.

III. RESULTS AND DISCUSSION

A. Bulk Periodicity under Floquet Conditions

All runs I performed under Floquet conditions used combinations of p and q that exhibited ballistic spread in the limit $T \to \infty$. The initial Floquet condition runs used T = 5, which produced lightcones whose front velocities fell abruptly to 0.



FIG. 1. For a Floquet period of 5, the front velocity fell to 0 at seemingly random distances from the origin.

Upon inspecting the values of the q matrix at these sites, it was found that this front 'failure' occurred at sites where q = 1 for the number of timesteps equal to the length of the Floquet period; in other words, a site for which the 'death term' was active for T consecutive timesteps. The probability of this occurring is q^T , so the average length from the origin of this front failure should be q^{-T} sites. Clearly, this length grows exponentially in *T*, so tuning up Floquet period length quickly tunes the expected front failure length to orders of magnitude larger than the spatial system size. Since this event occurs only in a small regime, it can be considered rare. The rest of the Floquet runs were performed with periods close to 100.

One global feature of these Floquet runs was periodicity in the bulk. Again, rare events were seen in the low-Tregime, with some sites adopting a period of 2T instead of the driving period T.



FIG. 2. Higher harmonics seen in bulk patterning; several sites exhibit periods of 10 timesteps for T = 5.

When the Floquet period was tuned up, these were also suppressed so that every site in the bulk that exhibited patterning did so with a period equal to the Floquet period.



FIG. 3. Of the sites that had sufficient time to take on a periodicity, the period is equal to the Floquet period T.

The high-T regime also yielded a broader distribution of transient periods, defined as the number of timesteps it takes for a site to fall into its bulk pattern, counted after the lightcone reaches the site.



FIG. 4. A comparison of the transient period distributions for the low-T regime (upper figure, T = 5) and the high-T regime (lower figure, T = 100).

B. Front Velocity Separation

For a fixed p, q combination over a range of Floquet periods, front velocities varied in the low-p low-q range, but were identical in the high-p, low-q range. In the former regime, smaller Floquet periods resulted in a smaller front velocity and narrower lightcone than for larger Floquet periods, with some limit for velocity sparation at sufficiently high T.



FIG. 5. For p = 0.9, q = 0.4, front velocities are indistinguishable for a range of Floquet periods.



FIG. 6. For p = 0.4, q = 0.2, front velocities separate, correlating directly with Floquet period length up to a limiting T value.

A more extensive numerical study for this range of Floquet periods may show a similar separation in front broadening.

IV. CONCLUSION

The goal of this study was to extract universal behavior of quantum operator spreading using classical cellular automata, a class of discrete models in which the quantum effects of entanglement cannot be simulated. The rules governing the cellular automata models contained stochastic parameters, which were updated periodically in order to capture an essence of the time-translational invariance typically found in Hamiltonians in quantum systems. It was found that under these Floquet conditions, periodicity identical to the Floquet period emerged in the bulk of lightcones produced under all regimes of the stochastic parameters, and that the velocity of the front decreased with decreasing Floquet period for low ranges of these parameters. In a future study of this model, it would be interesting to analyze the effect of Floquet period variation for fixed p, q on the front broadening. On a larger scale, we hope that identifying global properties of quantum operator spreading through models like this will aid in studies on charge and energy transport in physical materials that experience quantum effects.

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Electrospun Nanofiber Layers for Improvement of Face Mask Performance

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Abstract

Electrospun nanofiber or microfiber layers deposited on a textile substrate are tested for potential use in re-usable face masks. Combinations of different polymer micro or nanofibers (Cellulose Acetate, PVA/PMA, and PVA/PB) on multiple substrates (knit, woven, and nonwoven fabrics) are tested and characterized in terms of filtration efficiency, pressure drop, moisture and salt capture, and porosity. PVA/PMA and PVA/PB nanofibers required crosslinking because they are water soluble solutions. SEM images before and after filtration testing visualize fiber morphology and particle pickup. The combinations that had good filtration efficiency while still allowing for good breathability were CA on knit for 30 minutes, CA on nonwoven for 15 minutes, and PVA/PMA crosslinked with glutaraldehyde on knit for 30 minutes.

Introduction

Face masks have always been used as Personal Protective Equipment (PPE) in health settings to reduce the spread of viruses and bacteria. The COVID-19 pandemic dramatically increased the demand for face masks throughout the globe. With the great variety of reusable masks made of knit, woven, or nonwoven fabrics now commercially available, ensuring the efficiency of these materials is essential for public health.

Knit, woven, and nonwoven fabrics are made of fibers greater than 10 microns in diameter or fibers assembled into yarns, which only prevent larger particles from penetrating. To capture smaller particles like viruses, nanofibers are crucial because of the potential for slip flow at the fiber surfaces. Therefore, depositing a layer of nanofibers onto a textile substrate increases the filtration efficiency of the material. These nanofibers can be fabricated by electrospinning specific polymer solutions.

To ensure efficiency while still providing comfort, an ideal mask needs both good filtration efficiency and good breathability. Filtration efficiency is inversely proportional to the number of particles that penetrate the mask, while breathability is inversely proportional to the pressure drop produced by the mask. Too much moisture buildup is also prejudicial to breathability. These relationships are used in this study to compare the performance of different combinations of polymer solution, substrate, and electrospinning time.

Experimental Procedures

Materials

Cellulose acetate (CA) (average molecular weight (Mn) = 30,000, acetyl content = 39.8%), Dichloromethane (DCM), methanol, 98% hydrolyzed Poly(vinyl alcohol) (PVA; Mw = $78\ 000\ g\ mol-1$), Poly(methyl vinyl etheralt-maleic anhydride) (PMA; average Mw = $216\ 000\ g\ mol-1$), hexadimethrine bromide (PB, Mw = $4000-6000\ g\ mol-1$), surfactant Triton X-100 (p-tertiary-octylphenoxy polyethyl alcohol). The substrates used were commercially available knit, woven, and nonwoven fabrics, with characteristics listed in Table 1.

	Knit	Woven	Nonwoven
Structure	Interlock	Broadcloth	Spundbond
Weight	137 gsm	118 gsm	41.7 gsm
Fiber	Cotton	Mercerized	Polypropylene
Content		Cotton	
Thread	33, 39	146, 71	-
Count	Threads/cm	Threads/cm	
Provider	TestFabrics,	TestFabrics,	JoAnn Stores,
	Inc.	Inc.	Inc.

Table 1: Fabric Specifications

Preparation of Polymer Solutions

The polymers used were CA, PVA/PMA, and PVA/PB. CA solution was prepared at 12% weight/volume ratio polymer concentration in 4/1 volume/volume ratio Dichloromethane/methanol solvent mixture (Goodge & Frey, 2020). To prepare both PVA solutions, 10 wt % PVA was dissolved in 20 mL of DI-water in an oven at 95 °C for 3 hours. PMA was dissolved in 5 mL of DI- water in an oven at 95°C for 30 min and then mixed with the PVA aqueous solution to form a 9/1 PVA/PMA mass ratio. Triton X-100 was added to the spinning dope. The same mass ratio and procedure was conducted for PB, but it was dissolved in room temperature instead of placing it in the oven. Three drops of Triton X-100 were added to each solution to reduce the surface tension of water (Xiao, Chery, & Frey, 2018). All solutions were agitated in the shaker overnight.

Electrospinning

To deposit nanofiber layers onto the substrates, electrospinning was used. To setup the electrospinning process, the polymer solution is transferred to a 5 mL syringe and mounted on a syringe pump (Harvard Apparatus). The needle is connected to a voltage box. Finally, a grounded copper collector plate is placed at a specified tip-to-collector distance. By applying high voltage to the tip of the needle, the electrostatic forces overcome the surface tension of the polymer solution, forcing the liquid out as a jet. After a specified amount of time, the collector is rotated to ensure even deposition of the nanofibers.



Figure 1: Electrospinning Setup

The syringe pump is used to set the flow rate and the voltage box to set the voltage through the system. These two variables together with the tip-to-collector distance determine the morphology of the nanofibers produced. After multiple trials, the ideal electrospinning conditions for each polymer solution were determined and described in Table 2.

Table 2: H	Electrospinnii	ng Specifications
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	CA	PVA/PMA	PVA/PB
Humidity	40-70%	20%	30%
Voltage	17 kV	22 kV	22 kV
Flow rate	1 mL/hr	0.5 mL/hr	0.5 mL/hr
Tip-to- collector distance	12 cm	20 cm	20 cm

Because PVA/PMA and PVA/PB are humidity-sensitive polymers, they were spun in a glove box. The glove box allows for controlling humidity by running dry air through it.

Heat-Treatment and Glutaraldehyde Crosslinking

PVA/PMA and PVA/PB are water soluble solutions and therefore require further treatment to stabilize the nanofibers before running subsequent tests. Both solutions can undergo glutaraldehyde (GA) crosslinking where the samples are left on a desiccator with an excess amount of glutaraldehyde for 7 days. The PVA/PMA solution is also capable of crosslinking through heat treatment (heat) where the samples are left in the oven at 68°C for 24 hours.

Scanning Electron Microscope Imaging

The scanning electron microscope (Zeiss 141 Gemini 500 SEM) was used to examine the morphology of the nanofibers. ImageJ software was used to measure their diameters. Images of the samples were taken before and after filtration to visualize particle pickup.

Filtration Testing

To characterize the performance of the two-layered material created, the filtration testing setup (Figure 2) is used. A 38mm diameter circle is cut from the sample and mounted on to the filter holder. An animal respirator (Harvard Apparatus, Model #B-55172) running at 25 breaths/min and 50/50 inspiration/expiration ratio is used to simulate human breathing. A continuous air compressor (Medline Aeromist Plus Nebulizer Compressor, Model #MEDHCS60004) aerosolizes 1M NaCl solution which mixes with the exhaled breaths and passes through the filter. Any particles that penetrate the sample are counted by the particle counter (MetOne Instruments, Aerocet 531S) and separated between 0.3um, 0.5 um, and 1.0 um diameter. Particle counts (PC) data is then converted to filtration efficiency (FE) by particle size using the equation below:

$$FE(time) (\%) = \frac{PC \text{ no filter} - PC \text{ sample (time)}}{PC \text{ no filter}} *100$$

Throughout the 30-minute test run, a manometer records the pressure differential, maxing out at 350 cm water. The weight of the sample is taken before (initial weight) and after the test run (wet weight), as well as after it dries in the oven (dry weight). This data is used to calculate moisture capture (difference between wet weight and dry weight) and salt capture (difference between dry weight and initial weight).



Figure 2: Flat Filter Test Setup

Capillary Flow Porometer Testing

The porometer (Porous Materials, Inc., CFP-1100-AEHXL) was used to calculate mean flow pore diameter and mean flow pore pressure. Calwick with surface tension of 20.1 dynes/cm was used as a wetting agent.

Results and Discussion

After imaging the samples with the Scanning Electron Microscope, the nanofibers were, on average, 978 nm in diameter for CA, and 194 nm for PVA/PMA(GA). PVA/PMA(heat) showed some nanofiber structure, but fibers were fused together in almost a film-like structure. PVA/PB samples, however, did not have any nanofibers. They turned into a film; crosslinking was not successful. Figure 3 shows the fiber structures of each polymer as spun.



Figure 3: Fiber structures of each polymer as spun

On this account, PVA/PMA(heat) and PVA/PB were not executed on the nonwoven fabric.

Examining filtration tests, the first determining factor was pressure drop. Figure 4 shows the minimum and maximum pressure drop of one cycle of tidal breathing of each sample after it reaches a plateau. Because high pressure drops lead to low breathability, samples that reached the maximum limit of 350 cm water were automatically separated out.



Figure 4: Pressure Plateaus

After that, filtration efficiency data was used to compare the samples that had reasonable pressure drops. The samples that had the best filtration efficiency between each polymer solution are show in Figure 5. These samples were: CA on knit for 30 minutes, CA on nonwoven for 15 minutes, PVA/PMA(GA) on knit for 30 minutes, PVA/PMA(heat) on knit for 15 minutes, and PVA/PB on knit for 30 minutes.



Figure 5: Filtration Efficiency for select samples

To further compare the performance of the samples, wet and salt capture were tabulated in Figure 6. Samples CA on knit for 30 minutes and PVA/PB on knit for 30 minutes had moisture captures that were too high and could cause wearer discomfort.



Figure 6: Moisture and Salt Capture of Samples After Filtration Testing

Since the heat-treated PVA/PMA and PVA/PB did not have ideal nanofiber structures, the focus turned to CA and PVA/PMA(GA) samples. Samples of PVA/PMA(GA) on knit for 30 minutes showed more inconsistencies, with much higher standard errors throughout the test run than CA samples. Additionally, CA samples had higher filtration efficiencies overall, especially for larger particles.

CA samples were also analyzed with the porometer, and data is tabulated on Figure 7. PVA/PMA and PVA/PB did not interact well with the porometer and therefore the equipment was not able to produce data for them. The CA samples selected from before showed small pore diameters and low pore pressures, which is ideal. CA on nonwoven for 15 minutes had smaller pore diameter than CA on knit for 30 minutes but had higher pore pressure.



Figure 7: Porometer Data for CA samples

Overall, mean flow pore diameter decreased and mean flow pore pressure increased with increasing electrospinning time due to the thicker layer of nanofibers deposited.

Conclusion

The woven fabric produced high pressure drops for almost all polymer solutions and electrospinning times. Glutaraldehyde crosslinking on PVA/PB and heat crosslinking on PVA/PMA were not successful and did not result in viable nanofiber structures. CA samples behaved more consistently throughout the tests and even though PVA/PMA(GA) nanofibers had smaller diameter, their filtration efficiency was still lower than CA. Wet and salt capture data showed too much moisture buildup on CA-K30 and PVA/PB-K30 samples. The samples of CA on nonwoven fabric for 15 minutes performed better overall, with good filtration efficiency and breathability.

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Developing An Alternate Method for Locating and Classifying Imperfections in Crystalline Nanomaterials

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Transitioning to renewable energy is one of the most pressing scientific and technological challenges today. As the production of renewable energy increases, so must the capacity of large-scale energy storage technology. Lithium-ion batteries currently serve as the energy-storage unit of choice, but they present a challenge for future growth because of lithium's relative scarcity and associated rising cost. Sodium-ion batteries are a promising alternative to lithium-ion batteries, because of sodium's abundance and characteristics similar to that of lithium. However, sodium-ion batteries exhibit voltage fade after several charging cycles, leading to insufficient cycle stability for widespread use. There are several possible causes of this phenomenon, including decreased capacity due to dislocations in the structure of the sodium ion crystals. One method of studying crystal structure is Coherent X-ray Diffraction Imaging (CXDI), which is a lensless method of imaging that uses a coherent light source to pass through the given object, and produces diffraction patterns of the crystal structure which are read by a detector. Though the amplitude information is preserved, phase is lost in the process and both are needed to reconstruct the crystal. Current methods of reconstruction are time-consuming and difficult to use. Using computer simulations it is possible to observe the phase patterns of dislocations with varying geometries. Dislocations appear to be preserved within the phase pattern. This finding demonstrates that it is possible to develop a framework with which to view future reconstructions of crystals.

I. INTRODUCTION

Fossil fuels are the most commonly used source of energy worldwide. To make a smooth transition to using renewable as a primary source of power, large-scale storage systems need to be upgraded to meet the new demands of shifting from peak hours of energy-use to off-peak hours. A number of systems have been proposed but lithiumion batteries are of particular interest given that they have been widely used and optimized in the past years. They are currently the battery of choice for both electric vehicles and hand-held personal devices such as smartphones and tablets. Sodium has similar properties as lithium, because they are both alkali metals, but is far more abundant and provides a more cost-effective solution for large-scale implementation [1]. However, while sodium and lithium have similar properties, lithium has been shown to have a higher energy density (mass to energy ratio) and a longer life cycle, thus currently being favored over sodium-ion batteries[3]. Findings suggest that the voltage-fade in sodium-ion batteries has to do with partial dislocations in their crystalline structure [4]. Further study of these dislocations may provide more insight into the performance of these materials and lead to the development of commercially available sodium-ion batteries. However, capturing these crystal defects proves challenging because of the time-consuming nature of the reconstruction process.

Coherent Diffraction Imaging, (CDI) is used to study many things including biological structures and catal-

ysis, as well as for batteries. Using Coherent X-Ray Diffraction Imaging (CDI) it is possible to map the threedimensional diffraction patterns of crystalline nanomaterials via a lensless method. In order to reconstruct the structures, the amplitude information must be extracted from the scan and then a reconstruction algorithm is typically applied to the diffraction and it is changed parameter by parameter until a reconstruction of high resolution is achieved [6]. However, this process is time-consuming, and often goes through 1000's of iterations [5] so here we explore alternatives to the reconstruction process for locating and classifying dislocations within crystalline structures. Faster identification of dislocations will lead more time spent on the effects of the dislocations on the structures they are a part of. Here we present the beginnings of an alternate approach to the iterative reconstruction process via the identification of phase singularities in reciprocal space.

II. METHODOLOGY

As shown in Fig.1, we start by creating a cubic crystal in space, simulated as a three-dimensional matrix of 1's and 0's. Once the perfect crystal is created we can introduce a screw-dislocation of varying geometries using:

$$S(r) = s(r)e^{-iqu(r)} \tag{1}$$

where s(r) is a shape function known as the Ewald function where the value of the function is based on its position to the boundary of the volume of the crystal. It can

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FIG. 1. Panel A shows a cubic crystal with a sinusoidal wave dislocation confined to the y-z plane. Applying Fourier Transform produces a 3-Dimensional diffraction pattern which is depicted as an isosurface in part b. Part C depicts a 2-Dimensional slice through the center of the figure and Part D the 2-Dimensional phase through the center of the diffraction.

be described as follows [5]:

$$s(r) = \begin{cases} 1 & r \in V \\ 0 & r \notin V \end{cases}$$

the phase $\phi(r) = qu(r)$, where u(r) is the deformation field.

$$u(r) = u(x,y) = \frac{b\theta}{2\pi} = \frac{b}{2\pi} \arctan 2\left(\frac{y-y_0}{x-x_0}\right) \qquad (2)$$

Here b is the Burgers vector and z is fixed so the deformation field is only with respect to x and y. x_0 and y_0 are determined by the desired shape of the dislocation. For example, a spiral dislocation is introduced by using the z coordinates from the particle and applying the following:

$$x_0 = r * \cos(z * h) \tag{3}$$

$$y_0 = r * \sin(z * h) \tag{4}$$

where r is the radius and c is the helicity. Each shape uses a different equation and parameters. To simulate an xray passing through the particle we then apply a Fourier Transform to the particle, which provides the simulated nanocrystal's diffraction pattern as an S(r) complex function with real components. From the diffraction pattern we can obtain the intensity of the light at each point in space, which corresponds to the amplitude of the wave at that point. We can also find and plot the phase information as shown in Fig. 1 d.

After obtaining the necessary information, a number of methods were tried to circumvent the reconstruction process and obtain the locations and shapes of singularities within the crystal.

A. K-Means Clustering

One approach to locate singularities was the use of clustering algorithms for unsupervised classification of the clusters. We created a data set of 12 3-dimensional diffraction patterns containing a control with no dislocation, and a straight dislocation. The remaining diffraction patterns consist of helical screw dislocations with varying radii and helicity. Using the heuristic known as the "Elbow Method" to determine an ideal number of clusters, we applied K-means clustering to each of these nanocrystals. In addition to individual clustering of these particles, we also clustered them as an entire data set to observe possible characteristic properties in of screw dislocations as a whole. In Fig. 2, it is evident that the singularity is clustered with the background as expected. However, this method does not capture all of the singularities shown in the phase data and does not find singularities in nanocrystals containing screw dislocations with more complex geometries. Thus, this method is not robust and is non-ideal for identifying dislocations.

B. Computational Solving

Another approach to identifying singularities in nanocrystals was computational in nature. Using the Fourier integral for this system [5]:

$$S(q) = \int S(r)e^{-1q \cdot r} d^3r \tag{5}$$



FIG. 2. Panel A shows the diffraction pattern of a center sliced straight dislocation. Panel B shows the clusters of the data after being put through K-means clustering. The clusters show poor resolution and are not a robust method to isolate singularities.

We can rewrite this as a symbolic, definite integral in terms of x and y as follows:

$$\int_{\frac{-a}{2}}^{\frac{a}{2}} \int_{\frac{-a}{2}}^{\frac{a}{2}} e^{i(q(x+y)+r*arctan(\frac{x}{y}))} dxdy \tag{6}$$

Running this formula in Mathematica and python's Symbolab yielded null results. There were no valuable applications gained from this approach. However, this demonstrates that a simulation-based visual approach is more useful.

C. Phase Analysis

While this approach requires the phase retrieval algorithms to be used, the simulated data allows for a beginning to end analysis of the nanocrystal, creating the potential for a framework with which to reconstruct dislocations in real data. This approach is especially useful when the singularities are not clearly visible in the intensity data, because it would identify singularities that

FIG. 3. **a**, This panel shows the shape of the dislocation in real space, which is curved. **b**, This panel shows a slice of the 3-Dimensional singularity data. The curved dislocation is preserved in diffraction space and replicates outward from its origin.

would otherwise go unnoticed. For simplicity, we only used cubic nanocrystals and placed a maximum of one dislocation in the center of each. This data set used only screw dislocations, but included 5 different varieties of screw dislocation; straight, helical, sinusoidal, curved, and sloped. We used a modified version of the Iver-Grey method [2] for isolating phase singularities. Taking a line integral of four pixels around each point we are able to isolate the singularities in the nanocrystal as seen in Fig. 4. Mapping these singularities back onto the phase shows that the algorithm successfully locates all singularities for a given nanocrystal. It is also evident that this identification process happens regardless of whether the singularities are visible in the diffraction pattern. With this we are able to view the transition of the dislocation's geometry from real to diffraction space, thus allowing more insight into characterizing each dislocation's characteristic diffraction and phase patterns.



FIG. 4. This figure illustrates the ability of the singularity algorithm to accurately detect singularities in the phase when they are visible in the diffraction intensity pattern and when they are not.



FIG. 5. This graphic shows all of the shapes of dislocations in real space in comparison to portions of their singularity patterns in diffraction space. **a**, Cubic particle with a centered, sinusoidal screw dislocation in the y-z plane. **b**, Cubic particle with a centered spiral screw dislocation. **c**, Cubic particle with a centered linear screw dislocation at an angle. **d**, Cubic particle with a centered straight screw dislocation. **f**,Portion of the 3-Dimensional singularities present in reciprocal space for the wave dislocation . **g**,Portion of the 3-Dimensional singularities present in reciprocal space for the curved dislocation. **j**,Portion of the 3-Dimensional singularities present in reciprocal space for the curved dislocation.

III. OBSERVATIONS AND ANALYSIS

A natural extension of identifying singularities in two dimensional space is to plot the singularities in three dimensions, so as to understand how the shape of the dislocation changes. As seen in Fig. 3, the shape appears to stay preserved in diffraction space and replicates from the central peak out to the edges of the nanocrystal's environment. This is promising because it means that it is possible to classify the shape of a dislocation using only its phase pattern. As seen in Fig. 5, all five shapes studied held their shape in diffraction space. However, all shapes seem to preserve some characteristics of the straight dislocation in their singularity patterns.

IV. CONCLUSIONS AND OUTLOOK

Phase analysis appears to be a promising method for classifying and locating dislocations. However, this was a simplified approach to observe how dislocations appear in diffraction space. Further work must be done to examine if the shape-preservation effects extend to nanocrystals of more random shapes and to nanocrystals with more than one dislocation.

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I. Introduction

Cationic polymerizations offer the opportunity to create a wide catalogue of polymeric materials with complex architecture. Traditionally, these polymerizations were challenging since they needed to be done under low temperatures, inert conditions, and required rigorous purification of starting materials. The recent development of a single component cationic polymerization of vinyl ethers using pentacarbomethoxycyclopentadiene (PCCP) as the initiating acid opened up the possibility of conducting these polymerizations under ambient conditions¹. Furthermore, a hydrogen bond donor thiophosphoramide was found to catalyze this PCCP cationic polymerization of vinyl ethers².

Cationic polymerizations, such as the PCCPmediated one, are initiated using an external stimulus, such as light. Light as a stimulus has several advantages over other stimuli (mechanical, electrochemical), due to it being inexpensive and pro-ecological. It also would offer us the possibility of spatial and temporal control over these polymerizations.

Photoinitiated processes have increasing relevance in industry, especially in 3Dprinting. The generated polymers have properties of interest like good adhesion, oxygen and moisture tolerance³, making them applicable to the electronics, automotive, and adhesive industries⁴.

Current commercial UV resins cure in about 6 seconds⁵, so the system would need to be optimized to make it more competitive for industry. Polymerization kinetics relate directly to low nucleophilicity and ion pairing⁶, so we hypothesized that the PCCP-mediated polymerization would be faster once the system was extended to different weakly coordinating anions. Using increasingly weakly coordinating anions like Cl⁻, PF₆⁻, and SbF₆⁻, we designed an increasingly faster cationic polymerization with light as a stimulus.

II. Synthesis

Synthesis of PCCP 7

Dichloromethane (84 mL) was added to a flame dried round bottom flask. Dimethyl acetylenedicarboxylate (8.26 mL) and dimethyl malonate (7.67 mL) were then added. Pyridine (0.275 mL) and acetic acid (0.255 mL) were dissolved in dichloromethane (1 mL), then added dropwise to the round bottom flask over 30 minutes. The solution was stirred at room temperature for 3 hours, yielding a reddish-brown color. After 3 hours, benzyltrimethylammonium chloride (5.18 mg) and a saturated solution of potassium carbonate (84 mL) was added to the round bottom flask. The reaction mixture was left to proceed for 16 hours. The PCCP precipitate was filtered and washed with dichloromethane (30 mL) and dried *in vacuo*. The solid was then dissolved in water (4 ml/g) and treated with HCl (2 ml/g) and left to dry *in vacuo*.

Synthesis of Iodonium PCCP

Iodonium chloride (206 mg) and methanol (2 mL) was added to a flame dried round bottom flask. A solution of silver PCCP (300 mg) and methanol was prepared in a separated vial, and added to the round bottom flask via syringe. The reaction mixture was left to go overnight. The solution then was filtered, washed with methanol and concentrated. The solid was transferred to a scintillation vial, concentrated, and dried *in vacuo*.

Synthesis of tris(3,5-bis(trifluoromethyl)phenyl) thiophosphotriamide (**HBD**)

3,5-bis(trifluoromethylaniline) (2 mL) was added to a flame dried 50 mL round bottom flask. Triethylamine (8 mL) was then added via syringe. The solution was cooled to 0°C with an ice bath, while thiophosphoryl chloride (0.39 mL) was added dropwise. The solution was then refluxed while submerged in an oil bath and heated at 100°C overnight. After completion, the solution was cooled to room temperature, diluted with dichloromethane (100 mL), and washed with NH₄Cl (saturated aqueous, 3 x 100 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated, yielding a yellow-reddish oil. Purification via column chromatography (SiO₂, 5% EtOAc/hexanes) yielded the product as a white solid. The product was further purified by recrystallization from hexanes.

Polymerizations using Isobutyl vinyl ether (IBVE), Iodonium Species (PAG), and HBD

Polymerizations were conducted using various amounts of HBD. Polymerizations were done in a UV reactor with 300 nm UV light. Solids were added to an oven-dried, nitrogen-filled reaction tube with a stir bar (PAG = 0.02mmol, HBD = .01/.02 mmol). IBVE (0.52mL, 4 mmol) was added through a septum via a needle syringe, and the reaction was initiated using a UV lamp.



Figure 1: Polymerization conditions for poly (isobutyl vinyl ether).

Polymerizations using camphorquinone, Ethyl 4-(dimethylamino)benzoate, PAG, IBVE, and HBD Polymerizations were conducted using different combinations of starting materials (Table 1).

	А	В	С
Camphorquinone (mmol)	0.02	0.02	0.02
Ethyl 4- (dimethylamino) Benzoate (mmol)	0.02	0.02	0
IBVE (mmol)	4	4	4
HBD (mmol)	0.02	0	0.02

Table 1: Different combinations of camphorquinone and ethyl 4-(dimethylamino) benzoate in polymerizations

Polymerizations were done using 456 nm blue light. Solids were added to a nitrogen-filled dram vial with a stir bar (Camphorquinone = 0.02 mmol, Ethyl 4-(dimethylamino) Benzoate = 0.02 mmol, PAG = 0.02 mmol, HBD = 0.02 mmol). IBVE (0.52 mL, 4 mmol) was added through a septum via a needle syringe, and the reaction was initiated using a blue kessil lamp. HBD (0.02 mmol, 15 mg) and diphenyliodonium hexafluoroantimonate (0.02 mmol, 12.9 mg). It was expected that using one equivalent of hydrogen bond donor along with a weakly coordinating anion for the photoacid generator would result in the fastest polymerization. Decreasing the nucleophilicity of the anion may allow for a stronger Bronsted acidity in the acid formed during photochemical decomposition of the onium cation, accelerating the kinetics of the polymerization.

As the polymerizations increased in speed, they became difficult to observe and measure quantitatively, so the experiment with iodonium hexafluorophosphate was the fastest quantitatively observed experiment.



Figure 3. Conversion of IBVE versus time using different anions for the PAG



Figure 2. Polymerization conditions for poly (isobutyl vinyl ether) using camphorquinone/amine initiator system

III. Results and Discussion

Poly (isobutyl vinyl ether) was polymerized using several different anions **IV.** Conclusion The results of these experiments agree with the hypothesis that a hydrogen bond donor can catalyze the polymerization of isobutyl vinyl ether and that this polymerization can be initiated using light as a stimulus. This catalytic system provides future opportunity to further increase and investigate the kinetics of this photoinitiated polymerization by careful design of the PAG and HBD interaction.

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Strain mapping of quantum dot super-lattices using 4D-STEM

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Abstract

Quantum dot super-lattices that have epitaxial connections are a developing system of quantum materials. Super-lattices provided another knob in which to tune electronic properties. The electronic properties are still limited in part due to defects in the connections, which limit charge delocalization in the super-lattice. In this work we used 4D-STEM and the Cesptrum transform to map the local strain in a super-lattice of PbSe quantum dots. We observed strain defects in the necks of a super-lattice of PbSe quantum dots.

1 Introduction

Quantum dot super-lattices have potential applications in designer electronics and tunable band structures[1]. Creating a super-lattice of quantum dots provides another knob in which to tune electronic properties. The epitaxial connections in this system provide for electron coupling between quantum dots. In an ordered system there is charge delocalization in the super-lattice. Multiple factors cause defects in these materials limiting charge declocalization, such as orientational disorder, positional disorder and strain in the connections between dots. In this work we focused on mapping the strain in these connections, which can limit the electronic coupling and charge delocalization[2].

Quantifying this strain locally allows for a local understanding of defects and the ability to observe what relaxation methods are most effective. One limitation is getting accurate information from dots that have a large amount of orientational disorder. The method used in this paper access strain information from some of these off axis dots.

In this work, we used 4D-Scanning Trans-

mission Electron Microscopy (4D-STEM). This technique has the potential to gather strain information from off-axis dots, which can allow for strain mapping on systems that have orientational disorder. Other potential systems to map strain using this method are more disordered systems such as 1-D wires which are a potential precursor to the quantum dot superlattice.

2 Methods

2.1 4D-STEM

The data used in this paper was acquired at room temperature, using the next generation EMPAD detector. As seen in Figure 1, the electron beam scans through the sample creating a diffraction pattern collected by the EM-PAD for every scanning position.



Figure 1: The scanning beam at one real space position creates a diffraction pattern detected on the EMPAD[3]

One can then use these diffraction patterns to reconstruct a High Angle Angular Dark Field(HAADF) virtual image seen in figure 2. Which shows our real space resolution for our strain maps.



Figure 2: The full view virtual HAADF image of the super-lattice of quantum dots, collected on the EMPAD

2.2 Computation

In order to gather strain information from this data the Exit Wave Power Cesptrum (EWPC) transform technique was used[4]. This involves performing a Fourier transform of the log of each diffraction pattern, which creates a real space EWPC pattern. You can see this transform in figure 3 of a single diffraction pattern: $\mathcal{F}(log(|DP|^2))$. From the EWPC pattern it is possible to directly compute strain information.



Figure 3: (a is the diffraction pattern of one scanning position, the red circle denotes the (2,0,0) Bragg disk(b is the EWPC transform of that diffraction pattern

Figure 3 is an example of an EWPC pattern from a diffraction pattern of a single scanning position. Computationally the EWPC peaks can be tracked throughout every scanning position which we use to compute the strain information. The rotation map is calculated by the rotation in both of the selected peaks. The $\epsilon 11$ map is calculated by the compression and expansion of the first selected peak, which is the tensile strain in that direction. The $\epsilon 22$ map is calculated by the compression and expansion of the second selected peak. The $\epsilon 12$ map is the shear strain, and occurs when there is a rotation and compression in one peak but not the other. The absolute values of the strain are calculated with respect to an ideal reference lattice.

3 Results

Figure 4 shows the complete strain map for the calculated strain tensor. The virtual HAADF shows the selected region that was mapped. In this figure there is tensile strain in the $\epsilon 11$, which is observed in the neck. There is also a rotation between two dots observed in the θ map. A mask was applied in the strain maps for strain values over 15%. These values are due to the amorphous carbon the quantum dots are on, creating a pattern that does not have distinct EWPC peaks. It is possible for a peak to be in one primary direction but not the other, which explains the necks that exist in the $\epsilon 11$ map but not the $\epsilon 22$ map, even though there is no strain in that $\epsilon 11$ neck.

The resolution in the strain map is limited by the number of real space scanning positions



Figure 4: The full strain map of the selected region. Notice the tensile strain in the $\epsilon 11$ map and the rotation between the two dots in the θ map

and the convergence angle, which can be visualized as the resolution in the virtual HADAF.

3.1 Limitations

Figure 5 is an example of a diffraction pattern in a quantum dot that does not produce an accurate strain map. The EWPC peaks are smeared such that there is no reliable strain information from them. This region would need to be masked in a strain map.



Figure 5: (a is the diffraction pattern of one scanning position (b is the EWPC transform of that diffraction pattern

In order to achieve accurate strain maps smaller regions were selected in order to not avoid dots with unusable EWPC patterns. For larger fields of view that would contain these patterns masking of the EWPC patterns is necessary. This technique is able to look at some off-axis dots, but for a sample that had a large about of orientational disorder this method is not ideal.

The other major limitation is in the real space resolution. In order to have diffraction patterns usable for this method, the Bragg disks cannot overlap[4]. This sets a limit on the convergence angle needed to achieve this separation, which sets a limit of the real space resolution that can be achieved.

4 Conclusions

This project was able to use this method to map strain successfully over small fields of view. In order to achieve larger fields of view, masking is required for dots that have too much orientational disorder such that the EWPC peaks cannot be fully defined. Potential applications for this technique are for super-lattices that have many off axis dots, but still enough order for a successful map. We are looking at 1D-wires of PbSe quantum dots as a potential application for this technique. 1D-wires are a more disordered system and are scientifically interesting due to the possibility that they may be a precursor to the super-lattice. We are also interested in performing in-situ heating on this system to observe how the strain in the system relaxes under heating.

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Actuation of Iron Nanoparticle-Based Magnetoactive Elastomers in Spatially-Varying and Uniform Magnetic Fields

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Abstract

Magnetoactive elastomers (MAEs) are composite materials consisting of a soft elastomeric matrix embedded with magnetic micro- or nanoparticles. In a magnetic field, MAEs can both experience a change in elastic modulus and undergo large deflections. Much of the previous research has focused on the stiffening of MAEs with embedded microparticles and on their deflection mostly in a magnetic field gradient. In this paper, we explore the deflection of magnetic nanoparticle-based MAEs under both applied magnetic field gradients and uniform magnetic fields. We demonstrate that actuation is achieved under both field conditions and that nanoparticle concentration and alignment affect the magnitude and shape of these deflections. We also demonstrate a potential application of MAEs by exhibiting a programmable, refreshable Braille tactile interface.

1. Introduction

Magnetoactive elastomers (MAEs) are a type of composite material consisting of an elastomeric matrix embedded with magnetic micro- or nanoparticles. MAEs are notable in that various properties can be altered or enhanced under the presence of a magnetic field. One of the more commonly studied properties is the tunable elastic modulus of MAEs^[1,2]. The enhanced stiffness caused by an applied magnetic field has allowed MAEs to be utilized as 'smart' vibration dampeners and tunable load bearings.

Another emergent property of MAEs is their actuation that is enabled via the application of a magnetic field. Through the use of a soft, thin elastomeric matrix, the forces and torques applied to the magnetic particles within the material are able to deform the macroscopic shape of the film. This property highlights MAEs as promising candidates for magnetically controlled actuators to be used for valves or haptic interfaces^[3]. Our study is specifically focused on the creation of refreshable and deformable touchscreens.

Few studies have focused on the actuation of MAEs^[4,5]. Also, we observed that the majority of previous studies utilize magnetic particles on the micron-scale. We believe that using smaller particles will allow for finer precision in controlling deflections. Additionally, past studies have focused on

achieving film deflections through the application of a magnetic field gradient but have not yet explored the actuation possible in uniform magnetic fields^[4, 5]. By applying a uniform field instead of a gradient, a torque, rather than a force, will be exerted on the nanoparticles. We believe that this torque and the resulting rotations of the nanoparticles could present another method of obtaining large deformations in MAEs.

In this paper, we present the fabrication of MAEs using iron nanoparticles. We then measure the deflection of the MAEs under different magnetic field magnitudes and gradients. We report significant improvement in the actuation of MAEs in a magnetic field gradient, especially in the case of isotropic nanoparticle arrangements^[4]. Additionally, we provide a demonstration of a reconfigurable haptic interface using an MAE and magnetic field gradients. Finally, we include observations of film deflection under the application of a constant magnetic field.

2. Experimental Section

2.1 Fabrication of MAE Films

To produce the MAE films, iron nanoparticles (99.7+% purity with an average reported size between 40 and 60 nm) were combined with Smooth-On Eco-Flex 00-30 silicone rubber and Silicone Thinner. Films of four different magnetic nanoparticle concentrations were made: 2, 4, 6, and 8 percent by volume (vol%). Once the components were mixed, the sample was cured in a mold either in open air to allow random dispersion of the nanoparticles within the matrix (isotropic arrangement) or in a uniform magnetic field applied perpendicular to the face of the film so that the nanoparticles formed chains parallel to the applied field (anisotropic).

2.2 Characterization

Magnetic properties were measured using a vibrating sample magnetometer (8600 Series VSM from Lakeshore Cryotronics). Fields from -1.5 to 1.5 T were applied to record the M vs H hysteresis loops of the samples.

Tensile tests were performed via dynamic mechanical analysis with a TA Instruments DMA Q800. Isotropic samples of all four concentrations and a sample of pure silicone rubber were cut into thin strips. The strips were then stretched to strains up to 150% and the corresponding stresses were measured.

2.3 Deflection Measurements in a Field Gradient

The films were placed flat on an aluminum plate with a central 1 cm hole to allow the film to deflect only in a specific region. Vacuum was applied to secure the sample to the plate. A Zelux monochrome 1.6 MP CMOS compact scientific camera (Thorlabs CS165MU). Thorlabs mounted on three **TMS50-Z8** motorized translational stages (to allow 3dimensional spatial adjustment), was focused on the center of the film. Next, using a movable stage, two NdFeB block magnets were placed behind the film and moved towards or away from the film to vary the magnetic field and gradient at the sample's surface. After each movement, the camera was refocused, and the displacement was recorded. Two "movement loops" were performed where each loop increased the field from 0 mT to \sim 300 mT and then back down to 0 mT. The first loop magnetized the sample and the second was used to measure the response of the previously magnetized film. Measurements were taken for three samples of each concentration and particle arrangement (24 in total).

2.4 Deflection Measurements in a Uniform Magnetic Field

The sample was placed between two aluminum plates of a fixture with central 1 cm holes to allow deflection perpendicular to the face of the film while maintaining zero displacement at the edges. The sample was then placed in the gap of a custom-made C-shaped electromagnet such that the produced magnetic field was parallel to the face of the sample. The same camera and 3D motor setup was used to focus the image on the sample and measure displacements. However, due to less uniform deformation, deflection measurements were performed at seventeen different locations on the film rather than just one central location. A magnetic field was then applied from 0 mT to 400 mT and then back to 0 mT, with measurements being taken at 100 mT increments. The measurements were recorded after the sample had been magnetized up to 400 mT. The surface of the sample at each magnetic field level was then reconstructed in a 3D plot.

3. Results and Discussion

In a magnetic field gradient, films of all concentrations and either particle arrangement deformed uniformly with peak deflection the center of the sample. occurring at Additionally, all samples experienced macroscopic deformations under a field gradient. At almost 300 mT, the films deflected between \sim 800 microns (for anisotropic 2 vol%) and \sim 1670 microns (for isotropic 8 vol%). Also, all samples very nearly relaxed to their original shape upon removal of that field with almost all samples returning to within 60 microns of their initial location (Fig 1). In the isotropic case, the deflection measured represents an improvement of over 1700% of that reported in Marchi et al.^[4] This demonstrates that MAEs can macroscopically and reversibly deform upon application and removal of magnetic fields.



Figure 1. Film deflection as a function of magnetic flux density for the four nanoparticle concentrations for both a) isotropic and b) anisotropic particle arrangements.

Additionally, our data suggest that at least two factors affect the amount an MAE deflects in a magnetic field gradient oriented perpendicular to its surface. First, it is evident that our isotropic samples deformed more than their anisotropic counterparts. Returning to Figure 1, the average deflection of isotropic samples was greater than that for the anisotropic films of the same particle concentration at every concentration, ranging from a difference of 36% at 2 vol% to 64% at 8 vol%. We believe that this discrepancy is due to the soft magnetic nature of the nanoparticles. In the isotropic case, the particles are uniformly dispersed in the matrix and limited interaction between the particles allows the moments to align freely with the applied magnetic field. However, for the anisotropic films, the nanoparticles are closely bound in chains and thus align in head-to-tail formations because of the interactive forces between them. As the film deforms, the chains remain perpendicular to the surface but are no longer in line with the applied field and thus a weaker force is exerted towards the magnet, leading to less deflection.

Furthermore, for both isotropic and anisotropic samples, average maximal deflection increases with nanoparticle volume percentage. However, this increase appears to plateau at around 6 vol% (Fig. 1). For the isotropic samples, the increases from 2 to 4 vol%, 4 to 6 vol%, and 22.83%, 17.27%, 6 to 8 vol% were and 4.93%, respectively. In the anisotropic samples, the increases were 13.20%, 10.08%, and 0.67%, respectively. The reason for this behavior is related to the rates at which stiffness and magnetization increase with nanoparticle concentration. As displayed in Figure 2, the Young's modulus increased with nanoparticle percentage at a sharper rate than the magnetization recorded at 100 mT. Because enhanced magnetization increases the force and hence deflection, while increased stiffness dampens deflection, the increases in maximum deflection will diminish as nanoparticle concentration is increased. This will lead to a plateauing of the deflection as concentration rises, exactly reflecting the trend observed in Figure 1. As the gains become minimal after 6 vol%, we determined that this is the optimal nanoparticle concentration.



Figure 2. Young's modulus and magnetization at 100 mT for various nanoparticle loading concentrations.

Additionally, we engineered a Braille haptic interface using our optimally designed MAE. Using an Arduino-controlled circuit, pushpull solenoids move six bar magnets up and down in a 3 x 2 array. When the magnets are moved close to the sample, the film deflects downwards and represents a Braille pip, while a magnet moved away from the sample leaves the film flat. By specifically controlling the movement of the magnets, Braille letters are able to be displayed in series on the same surface. Thus, the device represents a real-time reconfigurable display in which one can feel the Braille letters and intuit words (Fig. 3).



Figure 3. Demonstration of using an MAE in a Braille haptic interface. The images are displaying the letters a) 'R', b) 'E', and c) 'D' in series to form the word 'red'.

Finally, deflections were also measured for our optimal (6 vol%) films under an applied uniform magnetic film parallel to the face of the films. While smaller deflections were observed, the observed deformations demonstrated a novel actuation method for MAEs.

Two significant observations can be made from these data. First, as expected, the anisotropic film deformed more than its isotropic counterpart. The isotropic film experienced a maximum deflection of less than 100 microns while the anisotropic sample deformed up to 350 microns, 250% more than the isotropic case. Furthermore, as evidenced in Figure 4, the anisotropic film achieved higher deflection as the magnetic field is increased while the isotropic film was relatively unaffected. Because the applied field was uniform, only a torque, and no magnetic force, was exerted on the nanoparticles. For the anisotropic film, the magnetic moments were all aligned perpendicular to the magnetic field and thus the chains of particles experienced the largest possible torque. The chains then rotated collectively and distorted the film. For the isotropic film, however, the magnetic moments were randomly aligned and torques were then applied in diverse, competing directions, determining a smaller deformation of the film.

A second notable observation from Figure 4 is the complex actuation mode of the

films. Whereas the films deformed to create an approximately uniform hemisphere when a field gradient was applied perpendicular to the film's face, the anisotropic sample in this case deformed differently. As seen in Figure 4b, the peak of the deformation of the anisotropic film is not central as one side of the film rose more than the other. Again, this behavior can be attributed to the actuation method as the rotating chains of nanoparticles twist the film into its deformed state rather than simply stretching it directly into its actuated state. This confirms the results obtained by FEA simulations performed by our group.



Figure 4. Surface reconstruction of a) isotropic and b) anisotropic films, both with 6% nanoparticles by volume, under various uniform magnetic fields.

4. Conclusion

Deflection of MAEs was achieved via two methods of actuation. Large, uniform deformations were observed upon the application of a field gradient perpendicular to the film surface while lesser and more complex actuation was measured in the presence of a uniform field parallel to the film surface. Additionally, for all samples in both field arrangements, the film returned close to its original undeformed state upon the removal of the applied magnetic field. These properties allow for the development of magnetically programmable. refreshable interfaces where shapes can be obtained upon application of a field and, upon removal of that field, disappear and allow the surface to return to the initial state. Our Braille display represents an example of an application of MAEs as haptic interfaces for the visually impaired. We aim to increase the resolution and precision of these deformations to be able to recreate a wider variety of more complex shapes.

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Novel and Sustainable Acid Catalyzed Synthesis of Conjugated Microporous Polymers

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Introduction:

Conjugated microporous polymers are a subclass of porous organic polymers with a promising potential in applications such as catalysis, gas separations, energy storage, chemoreceptive sensing, and organic electronics. The combination of the highly π -conjugated structure (leading to semi-conducting behavior), chemical stability, high surface area, and tunable porosity attribute to their variety of promising next-generation functions. ^{1–3} Currently, all methods to make CMPs use expensive metals such as Palladium and Nickel. These methods include the Sonogashira-Hagihara coupling, Suzuki-Miyaura coupling, Yamamoto coupling, and Buchwald-Hartwig coupling. ^{1,4,5} The metals used in these methods leave residual metals which can hinder the CMP's ability to function as desired. ^{6,7} In addition to the high cost of the metals, these methods are prepared under solvothermal conditions increasing the manufacturing costs further. Due to the vast limitations stated above, there is a current high need to develop a new solvent free method to synthesize CMPs under mild conditions. ⁸

Prior research has investigated the synthesis of organic porous frameworks using isothermal conditions by reacting diacetylarenes with molten SiCl₅ and *p*-toluensulfonic acid. However, these products show residual carbonyl peaks indicating the desired product was not completely formed. ^{9,10} In contrast, the use of nitriles in reactions with molten Lewis acids has been widely developed to synthesize porous conjugated triazine frameworks. ¹¹ A recent study done at Cornell University, hypothesized the method used to make CTFs could be adapted to make novel and sustainable CMPS. The study utilized the aldol reaction to synthesize conjugated microporous polymers without the use of expensive metals under isothermal conditions. This

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reaction takes advantage of the acidic nature of the catalyst, $ZnCl_2$, in order to dimerize a methyl ketone into a α , β -unsaturated ketone. Following the dimerization, a cyclotrimerization can occur to form the desired product. The study successfully reacted 1,3,5-triacetylbenzene, TAB, with molten $ZnCl_2$ to form a polymerized conjugated microporous polymer. However, when reacted with other monomers such as TAPM, $ZnCl_2$ did not form a porous monomer. Thus, $ZnCl_2$ was limited to only forming CMPs with TAB and was also subject to harsh reaction conditions. Therefore, a compelling need was found to find low-cost strong acid catalysts that could react to form CMPs under mild solvent free conditions with a library of monomers. Here, we investigated the first use of Lewis acids as catalysts in such CMP reactions. We report the findings of reacting 22 Bronsted and Lewis acids with 1,4-diacetyl benzene including the data from IR spectra, PXRD, and BET surface area measurements.

Methods:



Figure 1. The reaction mechanism used to synthesize novel and sustainable CMPS using an acid catalysis.

40mg of 1,4-diacetyl benzene were added to three 12mm glass tubes. 10eq. of the acid catalyst was then added to the tube. The 12mm tubes were flame-sealed under vacuum at 100mTorr on a custom-built apparatus. The tubes were baked at the melting point of solid acid catalysts and the boiling point of liquid acid catalysts for 72hrs. The tubes were then allowed to cool to room temperature. The tubes were broken and washed with 24mL water. If starting material formed a precipitate with water, ethanol was used for the wash in place of water. The resulting solid was soaked in 3M HCl for 48 hours. The acid soak was then vacuum filtered and washed with 10mL water and 10mL THF. The remaining solid was soaked in 10mL of THF for 24 hours at room temperature 3 times. Following the THF soaks, the solid was soaked in 10mL

of acetone for 24 hours at room temperature 3 times. The resulting solid was dried and weighed. IR spectra, PXRD, and BET surface area were taken of the solid.

Infrared spectra were collected on a Bruker Tensor II IR spectrometer with a diamond Attenuated Total Reflectance (ATR) attachment. Surface area data were collected on a Micromeritics 3-flex gas sorption analyzer using ultrapure N₂ (99.999%) and a liquid N₂ bath. Brunauer-Emmett-Teller (BET) and Langmuir surface areas were determined by linear least squares regression analysis using the linearized forms of the BET and Langmuir equations, respectively. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Ultima IV diffractometer equipped with a Cu K_{α} source ($\lambda = 1.5406$ Å) and were baseline-corrected using OriginPro.

If PXRD showed peaks indicating residual starting material or salts remained in the solid, the solid was refluxed for 24 hours in 10mL of 12M concentrated HCl. The solid was then vacuum filtered and washed with water and acetone. The resulting solid was dried and weighed. IR spectra, PXRD, and BET data were then remeasured and recorded.

Results and discussion:

Following the limitations of reacting acid catalyst ZnCl₂, 22 acid catalyst were reacted with the starting reagent 1,4-diacetyl benzene to investigate a possible reagent that had the capability of forming CMPs with a library of monomers under milder conditions. The reactions were performed under solvent free, isothermal, conditions without the use of expensive metal catalysts.

Bronsted acids as shown in table 1 made up six of the acid catalysts with four acid catalysts yielding product. The Bronsted acids used were all strong Bronsted acids with pKA's <5. After completely the reaction, IR spectra data was collected for each sample examine if the



Figure 2. IR Spectra Data for Bronsted acids in comparison with starting material DAB.

residual carbonyl peak was present. As described above, a limitation present when using diacetylarene is an incomplete reaction containing residual α , β -unsaturated ketone.^{9,10} After collecting IR Spectra data for all samples, it was clear they all contained strong carbonyl peaks at 1672cm⁻¹ as seen in figure 2. It was determined that likely, the Bronsted acids did not undergo a complete cyclotrimerization reaction resulting in residual ketones. Following this conclusion, we determined that Bronsted acids were not strong enough catalysts to force a complete reaction with the starting monomers and thus were not adequate reagents to make novel and sustainable CMPs.

Catalyst	Temperature	Yield (%)	PXRD	IR	Langmuir (m^2/g)	BET (m^2/g)	рКа
D. LLCI	1 (0 0 0			-			_
Py∙HCl	160°C	10.6	amorphous	Strong	-	-	5
AcOH	110°C	-	-	-	-	-	4.75
ТЕА	110°C						0.52
II'A	110 C	-	-	-	-	-	0.32
MsOH	150°C	196.3	amorphous	Strong	-	-	-2
PhSO ₃ H	65°C	68.0	amorphous	Strong	Nonporous	Nonporous	-2.5
5	00 0	0010	uniorphicus	Strong	renpereus	rionporous	2.5
TsOH·H ₂ O	110°C	114.7	amorphous	Strong	-	-	-2.8
Fable 1. A complete analysis of reactions performed with Bronsted acids showing IR Spectra, PXRD, and BET							

surface area data.

In our investigation, 16 Lewis acids were reacted with DAB. 10 acid catalysts yielded product as seen in table 2. Lewis acids that did not yield any product include SiCl₄, Zn(NO₃)₂, Al(NO₃)₃, SbCl₅, Zn(OAc)₂, and Al(SO₃CF₃)₃. Figure 3 shows the IR Spectra data of the products. Starting reagents AlCl₃, Zn(SO₃CF)₂, ZnBr₂, FeCl₃, BiCl₃, and FeBr₃ shifted the carbonyl peak



Figure 3. IR Spectra Data for Lewis acids in comparison with starting material DAB.

from the starting 1672 to 1692 cm⁻¹ with minimal or no residual peak at 1672 cm⁻¹ showing the acid catalyst had reacted completely or almost completely with the DAB to form a new product. TiBr₄ and SnCl₂ had no carbonyl peak at all indicating a complete reaction. In contrast, AlBr₃ and TiCl₄ had strong residual carbonyl peaks at 1672 cm⁻¹. This indicated that these two Lewis acids

did not completely cyclotrimerize to form the desired product and are not adequate catalysts to form CMPs.

Lewis Acid	Temperature	Yield (%)	PXRD	IR (cm ⁻¹)	Langmuir (m^2/g)	$\frac{\text{BET}}{(\text{m}^2/\text{g})}$
AlCl ₃	200°C	46.5	Amorphous	C=O peak at 1692	398.2	345.9
AlBr ₃	100°C	60.9	Amorphous	Strong C=O peak at 1672	<1	<1
$Zn(SO_3CF_3)_2$	310°C	70.9	Amorphous	Small C=O peak at1692	153.8	101.4
TiCl ₄	125°C	74.4	Amorphous	Strong C=O peak at 1672	76.1	120.2
SnCl_2	250°C	78.0	Amorphous	Absent	<1	<1
$ZnBr_2$	400°C	96.7	Amorphous	Small C=O peak at 1692	791.4	626.7
FeCl ₃	310°C	105.3	Amorphous	Strong C=O peak at 1692	409.0	302.4
BiCl ₃	250°C	72.9	Residual BiCl ₃	Strong C=O peak at 1692	676.7	508.9
TiBr ₄	240°C	93.24	Amorphous	Absent	-	-
FeBr ₃	200°C	205.8	Amorphous	Strong C=O peak at 1692	383.8	279.5
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 Table 2. A complete analysis of reactions performed with Lewis acids showing IR Spectra, PXRD, and BET surface area data.

Following the IR Spectra measurement, a PXRD was taken of all products. All products were amorphous except for the product formed with BiCl₃, sample CMM-I-070-M. As seen in figure 4, the PXRD data of BiCl₃ measured residual peaks similar to those of the starting



Figure 4. Comparison of the PXRD of sample CMM-I-070-M before(left) and after(right) reflux.

material. This indicated that residual salts and staring material were left in the product after the washing procedure. This was confirmed by the percent yield of the product as seen in Table 2 which was greater than 100%. In order to remove the residual salts, the BiCl₃ product was subject to 24 hours of

reflux in 12M concentrated HCl. A PXRD was retaken and showed an amorphous product indicating the salts had been removed.

After taking PXRD data, the third test done to determine which Lewis acid catalysts reacted with DAB to form CMPs was a BET surface area. Table 2 reports the Langmuir and BET







IR and PXRD indicated the starting Lewis acid catalysts that reacted the best with DAB to form CMPs were ZnBr₂ and BiCl₃.

Due to the harsh conditions that are required to react ZnBr2 with DAB, BiCl3 was chosen as the champion Lewis acid catalyst and optimization with this catalyst was performed comparing time and equivalent. The data collected from optimization is shown

Figure 6. IR spectra data comparing 10 eq of BiCl₃ reacted for 72hrs and 1 eq reacted for 24hrs

surface area measurements for all Lewis acids. The highest of which are $ZnBr_2$ (Langmuir=791.4 m²/g, BET=626.7 m²/g) and BiCl₃ (Langmuir=676.6 m²/g, BET=508.9). This data indicated the nitrogen that the CMP is able to absorb indicating the level of porosity of the molecule as seen in the surface area graphs depicted in figure 5. This data as well as the

in Table 3. Optimization was performed using 1 eq., 5 eq., and 10eq., of the Lewis acid with



Figure 7. IR Spectra data of reactions with 1 eq, 5 eq, and 10eq od BiCl₃ for 48hrs.

reaction times of 24hrs, 48hrs, and 72hrs. The 24hr reactions with 5 eq yielded no product. With 10 eq, the reaction yielded 8.3% yield. Unfortunately, this was not enough product to run IR Spectra or PXRD. The 24hr reaction with 1 eq showed an IR Spectra as shown in figure 6. The data showed product peaks at only medium strength compared to the 72hr reaction with 10 eq. Based on this data, it was determined that 24hrs was not an adequate reaction time. Next, the reaction was attempted with 1, 5, and 10 eq for 48hrs. All three reactions produced strong IR peaks as shown in figure 7. However, 1 equivalent had a lower yield showing that

10 and 5 equivalents had more efficient reactions. All three reactions also had amorphous PXRD



with 5 eq and 10eq od BiCl₃ for 72hrs.

the table 3, it was determined that when 5 eq of BiCl3 was reacted with DAB for 48hrs it was efficient for a complete reaction. To complete optimization, reactions were run for 72hrs using 1 eq and 5 eq of BiCl₃. All reactions run for 72hrs showed strong desired IR peaks as shown in figure 8. However, the yield for 1 eq was significantly lower than 5 eq and 10 eq as seen in table 3. This allowed us to determine that using 1 eq was less efficient in forming product. When running PXRD for all samples, the 1 eq and 5 eq products showed

residual salts. This sample was then subject to a second reflux with 12M concentrated HCl. When PXRD was retaken, the 1 eq product showed an amorphous structure, however the 5 eq product continued to show residual salt peaks. Based on this it was hypothesized that the residual peaks are increasingly formed as time and equivalence increases. Therefore, the most efficient reaction time and equivalence was determined to be 5 eq for 48hrs.

Equivalence	Time (hrs.)	Yield (%)	IR (cm ⁻¹)	PXRD
1	24	40.5	Medium Strength	amorphous
5	24	-	-	-
10	24	8.30%	-	-
1	48	64.7	Strong	amorphous
5	48	62.4	Strong	amorphous
10	48	210.6	Strong	amorphous
1	72	95.2	-	residual peaks
5	72	56.3	Medium Strength	residual peaks
10	72	72.8	Strong	amorphous

Table 3. Complete data of optimization using starting reagent BiCl₃ using 1, 5, and 10eq for 24, 48, and 72 hrs.

Conclusion and Continuation:

Based on the data observed thus far in the project, the synthesis of conjugated microporous polymers with Lewis acids, in particular BiCl₃, overcomes many of the limitations in current methods. The methods presented are done isothermally without the use of expensive metals. The reactions show no residual carbonyl peak indicating a complete cyclotrimerization. Finally, the reaction occurs under milder conditions than ZnCl₂. In continuation of this project, the next step is to complete optimization by taking an IR of the BiCl₃ 1 eq 72 hrs. sample. Then the next step is to follow the method stated above and react BiCl₃ with a library of monomers in an attempt to see if this procedure overcomes the limitation present in previous research. The hope is that the acid catalyst will form CMPs with a library of monomers and will have promising applications in the future of energy storage.

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Embedded Nonplanar Bioprinting for Tissue Engineering Applications

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Abstract: In recent years, embedded bioprinting methods have allowed for high-fidelity bioprinting of materials such as alginate and collagen by utilizing a shear-thinning support bath as a scaffold for extruded material. The perpetual support that this method gives extruded material also allows for departure from traditional planar printing methods. In this work, we apply nonplanar bioprinting to create unique 3D-printed geometries for mechanical testing that mimic the properties of native tissues through shape mimicry. Additionally, we explore the limitations of nonplanar bioprinting using a syringe extruder and determine that significant smearing while printing at steep, downward angles limits the potential printing directions of embedded nonplanar bioprinting.

Introduction

3D bioprinting has enabled many new tissue engineering possibilities, especially the potential to produce functional organ structures in a research or clinical environment.¹ There is significant need for the tissue-engineered organs that bioprinting can make possible, as evidenced by the fact that in August 2021, the national organ transplant waiting list was over 100,000 individuals long according to OPTN (Organ Procurement and Transplant Network) data. However, bioprinting has a long way to go before it can begin to meet this need. One obstacle is that many commonly used bioinks such as alginate and collagen are liquids upon extrusion, requiring an external factor to solidify, such as divalent cations in the case of alginate or pH balancing and temperature change in the case of collagen. This makes it difficult to print in open air at high fidelity; however, the embedded printing technique opens the door for high-fidelity printing of these materials by printing into a shearthinning support bath that acts as a scaffold for the material, holding it in place after extrusion.^{2,3} Additionally, the support bath can be modified to incorporate chemical agents that causes the bioink to solidify, such as CaCl₂ or a buffering agent.

Because the extruded material is perpetually supported, embedded bioprinting is not restricted to planar printing. In the case of nonplanar printing, the extruder is not restricted to completing each *xy*-plane before moving upwards on the *z*-axis. Instead, the extruder can move in any direction. This allows curved and angled designs to be printed more cohesively and quickly (Fig. 1). However, since downward extrusion would disturb already-printed material by passing through space that bioink was previously extruded into, there must be limitations on nonplanar printing.



Figure 1: Schematic of planar printing of a curve structure (left) and nonplanar printing of the same shape (right)

In this work we aimed to quantify the limitations of nonplanar printing, particularly the directions in which it is feasible to print. Additionally, we applied nonplanar printing to create corrugated geometries for tensile testing. The corrugated designs used for tensile analysis were of interest because nonplanar printing allowed these designs to be printed such that they were totally cohesive in the direction of applied stress (Fig. 2a-c). Additionally, this shape mimics the microscopically crimped morphology of collagen fibrils in the body (Fig. 2d). This microscopic crimping gives collagen a strainstiffening property that is mimicked in our macroscopically corrugated structures.^{4,5}

Materials and Methods

Printing

Alginate bioink was dissolved at 4% w/v in deionized water. Black India ink (1% w/v) was added to improve visualization of the printed material. FRESH v2.0 support bath was prepared according to the procedure used by Lee et al.² First, 500 mL deionized water and 500 mL ethanol (200 proof) were mixed

and warmed to 40° C. 20 g gelatin (Fisher) was dissolved, followed by 2.5 g Pluronic F127 (Sigma) and then 1 g gum Arabic (Ward's Science). The solution's pH was raised to 7 and then lowered to 6.25 before stirring overnight, unheated. The coacervate was aliquoted to 50 mL tubes and centrifuged at 400 rpm for 5 minutes. The supernatant was poured off and the remaining material was mixed in 25 mL distilled water and combined before centrifuging at 1750 rpm for 5 minutes. The supernatant was poured off and the remaining material was centrifuged in water once more, and then once more in a dilute solution of deionized water and CaCl₂ (0.1% w/v). After this, the supernatant was poured of once more and CaCl₂ solution was added again before storing at 4° C. To prepare the support bath for printing, the 50 mL tubes were pipetted homogenize the mixture and the tubes were stored in a vacuum chamber with loosened caps for ≥ 15 minutes before centrifuging at 1550 rpm and adding to the printing vessels

An Ender 3 (Creality) printer modified with open-source Replistruder 3 hardware was employed to extrude the alginate.² In order to remove the prints, the gelatin bath was melted at 37° C and aspirated with a pipette. The prints were then washed with a solution of deionized water and CaCl₂ (2% w/v) and carefully removed for analysis.

Optical Analysis

We designed G-code files for optical analysis such that lines printed in different angles from the horizontal could be isolated and photographed to measure the diameters of the printed lines in ImageJ. All photos were taken at 4x magnification. Angles are measured from the horizontal. Positive angles are ascending, while negative angles are descending.

Mechanical Testing

Three types of samples were printed for tensile testing: one flat, one corrugated at 22.5°, and another corrugated at 45° (Fig. 2ac). After immersion in 2% w/v CaCl₂ solution, these were refrigerated overnight and allowed to come back to room temperature before testing. Tensile tests were conducted on these samples using a custom mechanical analysis device that returns force data during a loading and unloading cycle. The experiments ran to 20% strain and back to 0% strain. We converted this raw data into stress vs. strain curves using the measured dimensions of the printed structures.



Figure 2: (a-c) Flat, 22.5° corrugated, and 45° corrugated tensile testing structures. (d) Micrograph of rat collagen.⁴



Figure 3: (a) Cartesion plot of print angles vs. line diameters, (b) micrograph of a line printed at 90°, (c) micrograph of a line printed at -80°, (d) naked eye view of print containing (b-c).

Results and Discussion

We expected line diameter and morphology to change significantly based on the angle printed at, especially in the case of downward angles where the syringe needle moves past extruded material as it extrudes it. The results (Fig. 3) show no statistically significant difference between lines printed horizontally and lines printed at a positive angle. However, significant differences are seen for lines printed at negative angles. These lines are thicker and more irregular due to smearing of the line as it is extruded and as the needle travels away from it (Fig. 3a, c-d). These results show that lines printed at steep, negative angles are not suited for precise printing because print resolution is lost at higher line diameters or when line diameter is unpredictable. However, this effect is less significant at shallower negative angles such as -45° and -22.5°. As such, these angles were used in print designs for mechanical analysis.

The loading curves for the tensile testing samples show the expected trends based on the crimped structure they were designed to emulate (Fig. 4). The 45° sample is strainstiffening but is overall the least stiff because little force is required to unfold the deep corrugations. The 22.5° sample exhibited more linear stiffness across all strains, while the flat sample became less stiff at higher strains. These results show that the increased shape-tuning that nonplanar printing offers also improves the tuning of the mechanical properties of printed structures.

Conclusion

These results show that at negative print angles, interference from the extruder consistently smeared the extruded line, causing it to become rougher and thicker than at flat or positive angles. However, this effect was not too pronounced at shallow negative angles. These print angles were applied for the cohesive corrugated geometry, which was able to mimic the strain-stiffening properties of the collagen which inspired it at the 45° corrugation angle. In the future, we hope to create heterogeneous structures with multiple materials loaded with different types of cells to create functional structures such as heart valves by leveraging the improved control that nonplanar printing provides while remaining within the method's limitations.



Figure 4: Overlayed stress vs. strain plots for flat sample, 22.5° corrugated sample, and 45° corrugated sample.

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