Growth Towards Light:
Translation of Optical Inputs into
Mesostructured Outputs via Inorganic Phototropism

Thesis by

Azhar Iqbal Carim

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Azhar Iqbal Carim
ORCID: 0000-0003-36306872

ACKNOWLEDGEMENTS

A close friend recently told me that the "dessert" of generating a dissertation is the opportunity to write the acknowledgments. In fact, composing the text in this section is a pleasure that I first started contemplating well before I ever submitted any application for admission to a graduate degree program. Midway through my undergraduate studies I found myself fortunate enough to have already received the opportunity to work with many individuals that contributed to my growth both inside and out of science. As I received my degree and progressed through my doctoral work, this list persistently became ever longer. Now, as I place a coda on the doctoral phase of my career and at last bring the words to a page, I am in awe of all the amazing interactions I have had, the support I have received, the friendships forged, and the countless memories made along the way.

First and foremost, I am extremely thankful for my amazing family. They have always worked to provide me all the resources to succeed and shaped me into someone capable of pursuing a doctorate at Caltech. They encouraged me as I moved several thousand miles across the country to study in Pasadena and then consistently supported me, never wavering, throughout the years of my graduate work. I am extremely happy that they can know that I have earned a doctorate.

I am grateful for having high school science teachers that helped me build the knowledge and spark the curiosity that served as the foundation for all my subsequent studies. Kevin Meisner (AP Chemistry) and Steve Dail (AP Physics) were excellent instructors with a genuine passion for education.

As an undergraduate at the University of Michigan, I was lucky to join Stephen Maldonado as the first student in his new lab. I remember having our initial conversation in his

office as he first installed Windows on his office computer. He taught me electrochemistry and all the ins and outs of the lab himself. Then, as the group took shape, I was afforded a unique freedom to work independently and lead my investigations. As my projects advanced Stephen mentored me on how make figures, write scientific papers, and navigate the publication process. When I was choosing potential graduate programs Stephen suggested I add Caltech to the list. Stephen has an amazing ability to conceive a potential storyline and associated manuscript before any results are collected, enabling targeted research and motivating students to pursue the project with clear goals. Thus, a great amount of the success I had during my doctoral work can in part be attributed to the mentorship I received from Stephen.

The early edition of the Maldonado group was a close-knit, collaborative and supportive community, a group of friends who were also intense researchers: an amazing place to cut my teeth as a scientist. Michelle Chitambar was the first official graduate student and offered a model of effectiveness. Jhindan Mukherjee, our sole postdoc for a while, was always a friendly presence and free to talk about anything. Kevin Hagedorn joined the lab as a senior student and taught me several tips and tricks. I worked closely with the industrious Junsi Gu who helped greatly in carrying out *in situ* SERS work. Sean Collins was an extraordinary undergraduate and skilled electron microscopist, and was an indispensable collaborator in the discovery and analysis of ec-LLS growth. I met Jeremy Feldblyum when he was a young graduate student but he clearly already had the heart of a professor and provided me with all sorts of scientific and academic tidbits. Sabrina Peczonczyk helped keep me in line and her presence always helped make being in lab a good time. I look back fondly on many nights on South U with Sean, Jeremy and Sabrina. Wen Wen often provided a unique brand of humor. Justin Foley helped perform device measurements for the initial ec-LLS work and was a reliable source of levity and laughter in the lab. Eli Fahrenkrug joined the group soon after I left but was a great companion at many

conferences as we both studied electrodeposition as graduate students, and I had the opportunity to watch as he continued with the ec-LLS research, expanding the scope and taking the science to exciting new heights.

Bart Bartlett's group was established at Michigan at the same time as the Maldonado group and took the role of our "sister" group, in many ways an extension of our own. Together we shared equipment and supplies, discussed science, collaborated and celebrated. Tanya Breault, Xiaoguang Hao and Joe Yourey were early members of Bartlett group that I had the pleasure of getting to know and helped me in various ways.

My undergraduate projects often found me in the lab of Adam Matzger. Matzger would often make rounds, strike up a conversation, and provide advice and experimental help as if I was his own student. I am thankful for the assistance of Vilmalí López-Mejías and Kira Landenberger on the Raman systems and of Antek Wong-Foy on the XRD instruments.

Al Wilson, George Johnston and Steve Donajkowski in the Michigan Chemistry instrument shop all provided excellent expertise and helped me succeed in my research efforts despite my then limited skills as a maker.

I was extremely lucky to have the support of Roy Wentz, glassblower extraordinare who showed amazing dedication and generosity. I warmly remember sitting down with Roy at his desk to for a "R&D" session in which I would bring him my experiment and he would devise a solution, but only after first offering me a cold drink. Then, I'd often be reminded to come back just before four o'clock when I would find whatever we had just designed already full realized and almost ready to come out of the annealing oven.

Beverly Lange wore many hats as Michigan Chemistry's undergraduate coordinator and I am thankful for the cheer and support she provided in all of these roles.

When I first arrived on campus in Pasadena, I often heard the phrase "Caltech is a special place" yet did not understand what it meant: it seemed not much more than trite and cliché expression. However, as I complete my doctoral work, I have come to learn that this saying is understood to have a precise meaning: that Caltech is a place where dynamic, talented people are brought together and provided an amazingly open environment and immense and incomparable latitude to pursue their curiosities in whatever manner they see fit, resulting in the spontaneous production of fantastic innovation and scientific excellence. I am extremely appreciative of my adviser, Nate Lewis, who has always strived to maintain this ideal with marked dedication and persistence. He provided me with great freedom from the start and at the same time was ready and able to offer support whenever needed, and always supplied encouragement. Nate charts his own path towards his goals and encourages everyone he works with to do the same.

I am very thankful that Barbara Miralles joined the group before me as she has served as a constant presence throughout my tenure always being unbelievably great at doing everything the group needs to run. Barbara has been a consistent source of support and it is always good to know that she is just a phone call away. I look forward to dropping by her office to hang out and chat many more times in the future.

I was fortunate to have an excellent team serve on my doctoral committee. Geoff Blake acted as the committee chair and provided insightful critiques of my proposals. Prior to joining my committee, George Rossman welcomed me into his lab and openly provided me access to his Raman microscope and other analytical tools. He was always happy to provide instrument assistance, discuss science, and let me borrow optics whenever I needed them. As a member of my committee, I have greatly valued his genuine scientific interest and curiosity. Harry Gray has always been more than willing to provide support whenever I need it and I am deeply grateful

for his consistent eagerness to talk and always open office door as well as the energy and enthusiasm he brings to every meeting.

I am extremely thankful for the support afforded to me by Harry Atwater and his group. Much of my doctoral research, including all the science presented in this thesis, has been enabled by collaboration with the Atwater group.

When I first came to the Lewis group, I remember talking with different members to explore the science that was underway and when I met with Bryce Sadtler about the phototropic project I immediately knew what I wanted to work on. I am indebted to Bryce for providing me with an amazing foundation to work from and getting me started in the lab and on a path to success. He also opened his bench space to me, let me use all his experimental apparatus, helped me gather supplies, and introduced me to the self-organized structures subgroup, the LMI-EFRC and the Atwater group.

I was lucky to join the Lewis group as part of a large cohort and am glad today that Noah Plymale, Nick Batara, Michael Lichterman and myself are all doctors and friends.

Nick was my key partner for many years and a great friend. Together we spent countless hours in discussion as we strove to decipher the mysteries of phototropic growth. Nick helped me learn a great deal about photonics and electromagnetism. Only through the combination of his modeling and theory work with my experiments were all the advances and conclusions presented in this thesis made possible. Fortunately, each of us believed that the other had the more challenging part of the project.

Lichterman and I collaborated on wide array of projects over the many years we shared. I was impressed by Lichterman's ability to effortlessly move between initial investigations at amazing speed to rapidly ascertain the potential success and novelty of a project. I appreciated his dedication to the mantra of "work hard, play hard" as well his eagerness to take full advantage

of the excellent opportunities and flexibility afforded to us as graduate students. I remember late nights of synthesizing nanoparticles interleaved with trips to Mexican restaurants. Together we also traveled across the country presenting at scientific conferences while also making sure to explore the host city. Emblematic of Lichterman's straightforward and honest style, he coined the now common nickname for phototropic growth, "squiggles".

Fadl and I worked together to complete several projects investigating electrocatalysts for sustainable hydrogen production. At the start of my doctoral studies I had not considered doing such research but got interested and picked it up in large part by spending time working at the bench next to Fadl's. Fadl had an impressive ability to assess risk-reward tradeoffs that he leveraged to maximize productivity which now I see is clearly a part of my own scientific approach. I am thankful for Fadl's outgoing nature and broad network, as a result he kept me connected in and out of work and introduced me to a great number of ideas, people and places, and continues to do so today.

Jonathan and I were collaborators on series of squiggles investigations. Jonathan was extremely smart with a broad knowledge base, the very type of person someone first imagines when thinking of the name "Caltech". He was likely almost always the smartest person in the room yet was also always down to Earth and demonstrated intense humility. Jonathan was usually my go to person if there was something that I couldn't understand or explain or something that I needed to do but didn't know how. Fortunately for me Jonathan was extremely kind and generous and helped me out time and time again.

Though Jonathan arrived at Caltech and joined the group two years after Lichterman, Fadl and I, it has hard to remember a time when he did not feel like part of our class. Together we all explored Los Angeles, learned to precision cook steaks sous vide, kept up with college football, and potentially exceeded the maximum payload capacity of my car several times. At a

point, it felt the TV show *Friends*, where people would drop by unannounced and open the door to my apartment assuming they'd find the others hanging out. I feel extremely lucky to have found such a set of close, lifelong friends.

Jesús Velázquez passion and motivation were a pleasure to have in the lab. Jesús took me on my first tour of Jorgensen and helped me start using the facilities there and connect with the JCAP team. Jesús was always excited to discuss new science and consistently provided encouragement and optimism.

Stefan Omelchenko was an excellent office mate and consistently provided a lively presence and good conversation.

Manny Soriaga gave me a second home in the HetCat-S group in JCAP (the Soriaga group at Caltech). Manny was an exacting scientist and at the same time full of color and constant source of humor. He was a fan of outings and celebrations: I fondly remember First Friday lunches and spreads from Porto's. Manny had assembled a tight-knit group of bona fide electrochemists and surface scientists. Jack Baricuatro knows all the old school electrochemistry tips and tricks and always shows great kindness and willingness to offer assistance. Kyle Cummins was an excellent maker and was always ready to grab tools and help build or repair.

Dan Torelli and I both spent time in Manny's HetCat group and I appreciated his carefree and fun-loving demeanor both inside and out of work. We had many good times often alongside Fadl and Lichterman.

I was lucky to have had the opportunity to mentor Anjali Premkumar. We started working together at the end of her freshman year at Caltech and her talent was immediately obvious. She quickly pioneered the investigations of phototropic growth using plural optical inputs and her experimental work contributed largely to the data presented in this thesis. Anjali also brought uplifting cheer and enthusiasm into the lab each day.

Annelise Thompson and I worked together on several graphene projects. I admired her tremendous work ethic and constant commitment to achieving success. She had a great sense for planning science and then methodically executing to meet objectives. Today, I miss hanging out with Annelise and Jonathan late into the night, talking and devouring bowls of popcorn.

Ethan Simonoff started by working on the "trees" project and then branched out to eventually discover new insights into inorganic phototropic growth that informed our later work. He was also key in bringing initial modeling workstation online and functional. Ethan was a wonderful source of irreverence and boisterousness. Together with Jonathan, we had a great time exploring all the coffee shops in and around Pasadena.

I happy to have mentored and worked with Kat Rinaldi pioneering new *in situ* Raman investigations of surface science and electrocatalysis, as well as *in vivo* analysis of live cells. I'll always remember the day we realized that cells can move. Kat always displays a down to earth personality and relaxed nature that I always appreciated yet also has an awesome vivaciousness with the ability to stir up conversation in any room. She can also "bully" me and keep me check.

Mita Dasog and I worked together to image via electrodeposition the spatial profile of photocarriers in semiconductor microwires and quickly grew close. Mita was exceptionally talented, and when I met her, already very extremely accomplished, yet always maintained a great sense of humility. Mita was extremely industrious, and I enjoyed the company of another night owl. She persistently exhibited great kindness and was always open to invest time and energy to collaborate, work hands-on, and help others scientifically even if a return was not expected. Mita has provided me a great deal of support and served as a role model both academically and generally.

Sisir Yalamanchili worked with Mita and I on the microwire electrodeposition project and together as "Team B" we had a lot of fun as me moved the project along. Later, Sisir helped me often when I had questions on photonics, electromagnetism and associated computer modeling, and helped frequently with taking care of clean rooms tasks. He also believed in the "work hard, play hard" lifestyle and was always open to trying new things. Together, we worked many odd hours and found ourselves on many adventures as we became close friends. Sisir was also a consistent source of humor, delivering many quotable lines that will never be forgotten.

I worked with Paul Kempler at the beginning of his graduate career along with Mita and Sisir as he started to get his microwire projects off the ground. Paul was smart and productive as well as passionate and fun-loving: always great have around.

Mentoring and collaborating with Katie Hamann has been a great pleasure. I have tremendous respect for Katie's hardworking ethos, perseverance, and commitment to reaching excellence. I also admire that at the same time she manages to be compassionate, generous, and warmhearted. Katie has been a phenomenal partner, an ideal counterpart, and has always driven me to achieve and improve. I also appreciate that she is always there to provide support. I remember sitting with Katie outside of Red Door Café at the start of her first year, encouraging her to take a leap of faith and work on phototropic growth with me. She jumped in with both feet and immediately started making major advances with squiggs and never stopped, and along the way I gained a great friend. I more than enjoyed every part of this journey from seeing her set the record candidacy time, to remaining steadfast together through long nights of squiz, through AFM days with typing tests and sticky note alignments, and to many nights playing with the torch.

I first met Madeline Meier when I took her out to lunch alongside Jonathan and Katie on the first day of her summer rotation with the group prior to her first year. There, I remember

we first introduced her to squiggles as Jonathan told her to "picture a sea anemone". She did not start on squigz just then but after that lunch we did quickly become great friends, and so when several months later when she told me she intended to join the group and was enthusiastic about squigz, I was thrilled. Today, I am extremely thankful that I have been able to mentor Madeline. She is talented, resourceful, and always jovial. Only a few weeks into her first project we bet on a conference abstract, submitting our hypothesized results and analysis, and several months later I got to see her present a complete story at a national meeting before even giving her first group meeting. Moreover, I am very appreciative that Madeline signed on to so many adventures and antics including driving all around LA to get the right picture of a tilted palm tree, learning to make burnt tortilla syrup and designing UFO themed artwork for scientific publications. She also stuck with me in solidarity on the correct side of BI 115. Additionally, Madeline has always been willing to help with whatever task I suddenly find myself needing to complete, often with short deadlines.

I am also very grateful for the chance to come together with Katie and Madeline to form squigz team. It is an amazing experience to work as a single cohesive unit wherein the whole is truly greater than the sum of the parts and the magnitude of what can be accomplished is exponentially greater than what any individual can. Simultaneously, there is comfort in knowing that any task or challenge can be borne by the team and that each person is never alone. Additionally, being close friends outside of work meant that all time at task was enjoyable and often relaxed. Sisir Yalamanchili was also often an honorary member, with contributions both scientifically and socially. Together, we made the rounds of coffee shops and dumpling restaurants, viewed eclipses and meteor showers, and also completed the "hat" bet, amongst much else.

Sophia Cheng was an excellent collaborator. She was a great help taking care of many of our team's nanofabrication and clean room needs, performing ellipsometry analysis, and assisting with computer simulations of optical processes. I admired her relentless work ethic and enjoyed her company on many late nights.

I am grateful that Matthias Richter decided to join Caltech full time after initially working at JCAP as a visitor. He presents a combination of great smarts and knowledge, extensive experience, and helpful disposition that make him an invaluable resource. He has been exceptionally helpful in the setup and management of the computer systems for our modeling work as well as generating all the MATLAB code needed for data analysis. Recently, Matthias has often been the person I go to for whatever I need scientific help and am not sure of the solution.

Michael Mazza (S.S. Slammer, D.D. Detective, Zoom-Zoom) quickly fit in as a Noyes boy and has managed to keep that spirit alive with his unique jocularity and whimsy. I am grateful for all he has done to make fun happen outside the lab.

Sean Byrne is currently the newest person investigating phototropic growth. Sean is dependable and diligent and also jovial and I am excited to see him make new advances.

Kimberly Papadantonakis served simultaneously in many different roles in the group. Her position as staff in tandem with her history as a group alum often provided useful perspective in navigating the challenges of the day. Kimberly helped me with a wide range of tasks spanning from event planning to grant writing. She was always been supportive of me and consistently demonstrated strong personal desire and commitment to aiding both the professional success and personal well-being of every member of the group. I also always delighted that Kimberly shared the belief that achievements are meant to be celebrated.

I am thankful for the chance to interact with a series of excellent postdocs that provided support and acted as models of success: Shane Ardo, Rob Coridan, Shu Hu, Teddy Huang, Ke Sun, Sonja Francis, Matt McDowell and Betar Gallant. Many other fellow graduate students also contributed to making my graduate experience rich, memorable and rewarding: Emily Warren, James McKone, Joseph Beardslee, Matt Shaner, Adam Nielander, Jacob Good, Heather Audesirk, Victoria Dix, Erik Verlage, Katie Chen, Brian Chmielowiec, Paul Nunez, Chance Crompton, Josh Wiensch, Ellen Yan, Weilai Yu, Kathleen Kennedy, Mo Morla, Zach Ifkovits, Jackie Dowling and Jake Evans. Undergraduate Jackie Maslyn also deserves special mention. Additionally, I am appreciative of all the contributions Bruce Brunschwig has made supporting the group.

Throughout my doctoral studies, I held several desks amongst the different group'sn campus offices and enjoyed spending time in each with their own communities and atmospheres. My base was a large time in G135 Jorgensen where I enjoyed many spontaneous large group conversations as well as one member missing photo shoots. I also had the pleasure of working upstairs alongside Madeline Meier, Sophia Cheng and Matthias Richter, an arrangement that proved extremely beneficial for the advancement of squigz work. Additionally, I always enjoyed trekking over to Noyes 220 to relax at desk, hangout and chat.

I am very appreciative of all the help I got from Ryan Jones in designing (and then frequently redesigning), 3D printing, and machining a great number of cells for photoelectrochemistry and spectroelectrochemistry.

I must thank Rick Gerhart in the Caltech glass shop for his many years of help building photoelectrochemical cells. It was always a pleasure to head down to the shop and chat.

More recently, Nate Hart has joined the shop as an excellent addition and has been a great help as well. Additionally, Mike Roy in the instrument shop is always a pleasure to work

with and helped design and along with Steve Olson helped make a series of pieces to complement our electrochemical cells.

I was lucky to be a part of the DOE-funded "Light-Material Interactions in Energy Conversion Energy" Energy Frontier Research Center (LMI-EFRC) for a large part of my doctoral tenure. It was a great opportunity to be connected with a team of very smart people doing exciting science and attending the biannual meetings and weekly seminars was always fun. I am appreciative of all the work done by Carrie Hofmann, Jennifer Blankenship, Tiffany Kimoto and Lyann Lau managing this program and must especially thank Lyann for entertaining all my pizza requests in the final years of the center.

My time as a graduate student was heavily influenced by presence of the Joint Center for Artificial Photosynthesis (JCAP), a DOE Energy Hub. I spent a significant amount of time collaborating on JCAP projects and working in JCAP facilities. I am thankful for all the opportunities and resources JCAP provided as well as all the people that JCAP connected me with. I especially enjoyed spending Friday evenings with Carl Koval, Achim Lewerenz, John Gregoire, Michael Lichterman, Kyle Cummins, Chris Karp, Ryan Jones and many others. I would like to thank Mabby Howard for all her efforts managing daily operations at JCAP.

I humbled by the magnitude of people that enabled my journey. Thank you all!

Azhar I. Carim
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Pasadena, CA

ABSTRACT

Palm trees exhibit phototropic growth wherein physical extension of the plant guides the crown towards the time-averaged position of the sun to maximize solar harvesting. In analogous fashion, the directed growth and resultant nanoscale morphology of an evolving inorganic semiconductor deposit can be precisely defined in three-dimensional space using incoherent, uncorrelated light with spatially-invariant intensity. Maskless, photo-driven electrochemical deposition of semiconductor films generates highly ordered, periodic mesostructures with anisotropic, nanoscale features conformally over macroscale areas. This inorganic phototropic growth process does not utilize any physical nor chemical templating agents. Rather, as with natural phototropism, wherein the morphological phenotype expressed by an organism is a function of the light available in the habitat during growth, the precise mesostructures are set by the deposition illumination. Structural complexity and anisotropy result as consequences of inherent asymmetry in the light-material interactions during growth. Here, the morphological outcomes defined by specific illumination inputs are explored and the microscopic optical phenomena underpinning this physical recording of light information is interrogated via both experimental and computational methodologies.

PUBLISHED CONTENT AND CONTRIBUTIONS

Self-Optimizing Photoelectrochemical Growth of Nanopatterned Se-Te Films in Response to the Spectral Distribution of Incident Illumination

Carim, A. I.; Batara, N. A.; Premkumar, A.; Atwater, H. A.; Lewis, N. S. *Nano Letters*, **2015**, *15*, 7071-7076. DOI: 10.1021/acs.nanolett.5b03137

A.I.C. designed the study, conducted experiments, and wrote the manuscript.

Polarization Control of Morphological Pattern Orientation During Light-Mediated Synthesis of Nanostructured Se-Te Films

Carim, A. I.; Batara, N. A.; Premkumar A.; Atwater, H. A.; Lewis, N. S. *ACS Nano*, **2016**, *10*, 102-111. DOI: 10.1021/acsnano.5b05119

A.I.C. designed the study, conducted experiments, and wrote the manuscript.

Morphological Expression of the Coherence and Relative Phase of Optical Inputs to the Photoelectrodeposition of Nanopatterned Se-Te Films

Carim, A. I.; Batara, N. A.; Premkumar A.; May, R.; Atwater, H. A.; Lewis, N. S. *Nano Letters*, **2016**, *16*, 2963-2968. DOI: 10.1021/acs.nanolett.5b04999

A.I.C. designed the study, conducted experiments, and wrote the manuscript.

TABLE OF CONTENTS

LIST OF FIGURES