COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY
University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

March 1, 2018

Honorable Members of the House and Senate Education Committees
State Capitol
200 East Colfax
Denver, CO 80203

Re: Annual Report of the Colorado Higher Education Competitive Research Authority (CHECRA)

Dear Representatives and Senators:

Colorado Revised Statute §23-19.7-103(3) requires the Colorado Higher Education Competitive Research Authority (CHECRA), housed at the Colorado Department of Higher Education, to report annually to the Education Committees of the Colorado House of Representatives and Senate on research projects funded by the CHECRA in the previous calendar year. This letter reports on activities and projects funded in calendar year 2017.

The CHECRA was created to provide a source of matching funds for National Science Foundation (NSF) and other competitive federal grants that require or benefit from a state match. CHECRA funding has helped to bring significant research dollars to Colorado. CHECRA spent $1.5 million in 2017 to support six multi-year research grants that jointly are bringing over $60 million in research dollars to the state.

The following projects received CHECRA funding in 2017:

University of Colorado (CU)

1. In 2014, the NSF awarded the University of Colorado a six-year, $22.8 million grant to continue and expand its Soft Materials Research Center into a full Materials Research Science and Engineering Center (MRSEC), one of the NSF's most prestigious awards. This Center focuses on work related to DNA nano-science and liquid crystal frontiers, an area where the University of Colorado is among the leading authorities. The CHECRA has pledged $400,000 per year for six years; 2017 was the fourth year of funding.

2. In 2016, with CU Boulder as the lead awardee, the NSF awarded a $24 million, 5-year grant for the Science and Technology Center on Real-Time Functional Imaging (STROBE). STROBE brings together universities, national laboratories, industry and international partners to create a powerful new set of real-time imaging modalities. CHECRA has pledged $400,000 for five years; 2017 was the second year of funding.

Colorado School of Mines

3. The Colorado School of Mines, along with Colorado State University, is part of the Institute for Advanced Composites Manufacturing Innovation, a consortium of 122 companies, nonprofits, universities, and research laboratories that are partnering with the federal government to create a manufacturing hub focused on U.S. leadership in next-generation materials. Approximately $2 million of this grant to the consortium is a direct financial benefit to the School of Mines. Recognizing the importance of this large initiative, as well as the number of players involved, CHECRA has pledged a limited cost share of up to $100,000 per year for five years, beginning in 2015. CHECRA made the third of three payments of $100,000 in 2017 to the School of Mines.

4. The NSF renewed the Colorado School of Mines' Re-inventing the Nation's Urban Water Infrastructure (ReNEWIt) Engineering Research Center, a $5.7 million grant for which CHECRA agreed to provide a continued cost share of $400,000 per year for five years. CHECRA made the second of five payments in 2017. With this grant from the NSF, the School of Mines joins leading universities in tackling acute water problems and needed infrastructure changes in the West.

Colorado State University (CSU)

5. The Accelerating Innovation Research – Research Alliance (AIR-RA) project at CSU, with $1.6 million grant from NSF, is advancing research in cadmium telluride photovoltaics with the vision of making PV electricity a major source of energy. The CHECRA made the third and final payment of $132,000 toward this project.

6. Colorado State University received a $5.5 million Advanced Research Projects Agency-Energy (ARPA-E) grant under its rhizosphere observations optimizing terrestrial sequestration program. This work will improve predictions of soil greenhouse gas emissions and long-term carbon sequestration. CHECRA provided the first of three payments in 2017; the first payment was $125,384.

In addition to the payments listed above, the CHECRA committed up to $500,000 for cost shares for Major Research Instrumentation (MRI) grants received from NSF in 2017. It had not yet made these payments as of December 31, 2017, as the Board was to make a decision on the allocation of the $500,000 among awards received at its 2018 annual meeting. These grants provide higher education institutions with major instrumentation that supports the research and research training goals of the institution and are also used by other researchers regionally or nationally.

Appendices to this report include detailed information on each of the projects listed above. In addition to the millions of dollars in federal funding coming into the institutions and the state—and the impressive scientific results achieved under the projects—the research centers funded by CHECRA positively impact Colorado. As noted in the attached appendices, these benefits include support for graduate and undergraduate students, outreach to K-12 students and teachers, and economic development benefits from spin-off technologies and companies.

Following are some highlights of these benefits to Colorado:

- The University of Colorado's Materials Research Science and Engineering Center carries out a variety of education and outreach activities that aim to enhance science literacy and achievement in communities, ranging from the K-12 population to CU's undergraduate and graduate students. To date, the Center's K-12 outreach program has offered 2,450 classes to more than 90,000 K-12 students. The Center also continues its partnership with Arrupe High School.
- CU's STROBE works closely with companies in STEM fields, including Ball Aerospace, Cymber-ASML, Intel and IBM. These partnerships have resulted in industry support for student professional development, internships and employment for graduating students as well as technology and knowledge transfer.
- Colorado State University's work under the ARPA-E grant is promoting CSU as a drought research facility. There is currently no national research site in the United States for agriculture that provides consistent drought environments. The field site in Fort Collins is a particularly good location for drought experiments, and CSU hopes to leverage its favorable environment and research infrastructure towards a national research site.
- The Colorado School of Mines ReNUWIt Center carried out numerous STEM outreach activities for K-12 students and teachers in the Front Range counties, focusing on energy-water systems, and also collaborates with the City and County of Denver, the Urban Drainage and Flood Control District and Enginuity Engineering Solutions to evaluate impacts on urban flooding.

During calendar year 2017, the Authority received a single distribution of Limited Gaming Funds of $2.1 million. Interest earnings on those funds totaled $38,425 for a total income of $2,138,425 in 2017. Payments to institutions are shown in the Summary of Financial Activity in Appendix A. Total expenses were $1,557,384.

Thank you for your support of this ongoing research. We welcome any questions.

Sincerely,

Kim Hunter Reed, Chair

Attachments:

Appendix A: CHECRA Summary of Financial Activity, 2017
Appendix B: University of Colorado Science and Technology Center on Real-Time Functional Imaging (STROBE)
Appendix C: University of Colorado Soft Materials Research Science and Engineering Center
Appendix D: Colorado School of Mines Institute for Advanced Composites Manufacturing Innovation
Appendix E: Colorado School of Mines Re-inventing the Nation's Urban Water Infrastructure (ReNUWIt) Engineering Research Center
Appendix F: Colorado State University Accelerating Innovation Research – Research Alliance (AIR-RA)
Appendix G: Colorado State University ARPA-E

APPENDIX A

Colorado Higher Education Competitive Research Authority
Summary of Financial Activity - Calendar Year 2017

Balance Available January 1	4,139,533.55
Revenues	
Limited Gaming Fund	2,100,000.00
interest earnings	38425.24
Total Revenues	$ 2,138,425
Disbursements	
Colorado State University	
AIR-RA program $400,000 in total; $134,000 per year 3 years	132,000.00
ARPA- Egrant 3 payments	125,384.00
Colorado School of Mines	
Engineering Research Center Reinventing Urban Water ERC (renewal) $400,000 per year/5 years	400,000.00
DOE Advanced Composite Manufacturing Innovation $200,000 per year 5 years	100,000.00
University of Colorado - Boulder	
NSF MRSEC Soft Materials Research Center Liquid Crystal Frontiers; and, Click Nucleic Acid IRGs $400,000 per year/6 years	400,000.00
NSF Science and Technology Center on Real-Time Function Imaging (STROBE) award notification 5 payments of $400,000	400,000.00
University of Northern Colorado	
Other	
audit cost*	0.00
Total Disbursements	$ 1,557,384
Balance Available at December 31	$ 4,720,575

Financial Notes:
Department of Higher Education is in the process of completing the 2016 and 2017 audit.

Appendix B

NSF award to University of Colorado, Boulder (UCB)
NSF Award: 1548924
Title: Science and Technology Center on Real-Time Functional Imaging (STROBE)
Period of Performance: 10/01/2016 – 09/30/2021 ($24M over 5 yrs. pending satisfactory progress)
Total 2017 CHECRA Funding: $400,000
Award PI's: Margaret Murnane, Jianwei Miao, Rafael Piestun, Markus Raschke, Naomi Ginsberg

Project Overview:
Microscopic imaging is critical for discovery and innovation in science and technology, accelerating advances in materials, bio, nano and energy sciences, as well as nanoelectronics, data storage and medicine. Fortunately, all areas of imaging, from electron to visible to X-ray, are undergoing revolutionary advances. However, no imaging technique can address a critical question underlying much of science and technology in the 21st century: how local (nanoscale) and extended (mesoscale) structure and interactions determine the properties and function of a material or biological system. Opaque, scattering and disordered samples common in chemistry, materials, and biology present a formidable challenge using any imaging modality. Notable demonstrations aside, current microscopies are simply too slow to routinely image functioning systems in real space and time. This severely limits progress in science and technology.

The NSF STC on Real-Time Functional Imaging (STROBE) is addressing this challenge by integrating different imaging modalities with underpinning technologies – advanced algorithms, fast detectors, big data manipulation and hybrid/adaptive imaging. Unlike conventional approaches - where scientists develop different, stand-alone, imaging technologies to solve specific problems – STROBE will integrate different imaging modalities with electrons, X-rays and optical nanoscopy to develop transformative imaging modalities that address grand challenges in science and technology. STROBE will:

- Develop a new set of powerful, broadly applicable, accessible real-time imaging modalities using electrons, X-rays and light that can image disordered systems, implement dynamic imaging with a large field of view, with chemical and magnetic contrast, with atomic/molecular/nanoscale resolution. STROBE will push each imaging mode to its fundamental limits and also integrate them to reach beyond these limits.
- Address key challenges common to all imaging modalities: the need for more powerful image deconvolution algorithms, THz to X-ray and electron sources, fast/sensitive detectors, spectrally/spatially/temporally shaped electron/X-ray/light illumination fields, and the need to manipulate and visualize large data sets.
- Educate a diverse group of students for innovative STEM careers in the 21st century. Imaging science is inherently multidisciplinary, spanning computing, physics, engineering, materials, nano and bioscience. STROBE will develop and assess new multidisciplinary degree and professional development/entrepreneurship programs, with international and industrial collaborations and internships.
- Develop and assess best practices for broadening participation in STEM careers by implementing long-term programs optimized for women, Native American, Hispanic and African American students.
- Engage in multiple modes of knowledge transfer with industry, national labs, other scientists and the public.

The **Vision** of STROBE is to transform imaging science and technology of functioning nano-systems. The **Mission** of STROBE is to create powerful and broadly-applicable real-time nano-to-atomic scale imaging modalities to advance imaging science and increase access, that can be used to address grand challenges in science and technology, while building a diverse STEM workforce.
From STROBE's inception, our plan has been to integrate broadening participation into all our efforts, spanning research, education and knowledge transfer.

Project benefits to the state of Colorado (Include support for graduate and undergraduate students, outreach to K-12 students and teachers, spin-off technologies and companies):
STROBE brings several benefits to the State of Colorado and is very cognizant of the great opportunity this project represents for science, education, outreach to K-12 students and teachers, as well as spin-off companies and partnerships with existing local industry, universities and national labs. In the first 15 months of STROBE, the following activities benefitted the state:

- STROBE and CHECRA funds are supporting ≈15 students, postdoctoral scientists and staff in Colorado.
- Imaging techniques developed by STROBE are being adopted by small business. STROBE collaborations with Anasys and KMLabs has attracted two new STTR joint projects between Boulder scientists (Kapteyn, Murnane, Raschke) and industry to accelerate knowledge transfer.
- NIST Boulder laboratories is using technologies developed by the Boulder STROBE PIs (commercialized through KMLabs).
- STROBE is providing funds to Science Discovery at CU Boulder to augment K-12 workshops for students and teachers that are delivered around the State of Colorado, including the four-corners region.
- STROBE provided letters of support to Fort Lewis and Mines for large NSF proposals.
- STROBE was part of a PREM proposal for Functional Nanomaterials, involving a strong partnership between Fort Lewis College (Durango, lead organization), with Norfolk State University and STROBE. This collaboration integrates education, research and broadening participation across FLC, NSU and STROBE.
- STROBE industry members Ball Aerospace (Boulder) and Cymer-ASML (San Diego) are providing funds for student professional development and innovation competitions.
- STROBE is offering unique professional development opportunities for students in project and people Management and Leadership, that are not usually offered to students in the Physical Sciences and are attracting non-STROBE participants.
- New transdisciplinary graduate programs in imaging science are now available at CU Boulder, to better prepare students for the 21st century workplace, with students already enrolled.
- STROBE is developing methods to characterize samples provided by Intel, Ball, IMEC, IBM and elsewhere, that are challenging to characterize using other techniques. These bring many opportunities for students for internships, permanent positions and for knowledge transfer.
- A diverse set of 11 graduates were hired by US National Laboratories and Industries.

- Colorado students and faculty won many prizes, awards and fellowships. CU Boulder graduates Dr. Dennis Gardner won the American Physical Society Laser Science Thesis Award, Jennifer Ellis was awarded an NRC Postdoctoral Fellowship to work at NIST Boulder Labs, and Nathan Brooks was awarded an NSF Fellowship. Fort Lewis faculty Dr. Megan Paciaroni received a major NSF MRI grant. Boulder faculty Markus Raschke was elected Fellow of the American Association for the Advancement of Science, Noah Finkelstein received an NSF INCLUDES Grant, and Margaret Murnane was awarded the OSA Ives Medal (highest award of the Optical Society of America).

2017 STROBE Highlights (STROBE.colorado.edu):
In the first 15 months of STROBE, we published 14 papers in the top peer-reviewed journals (including 2 in Nature, 1 in Science, 1 in Nature Photonics and 1 in Nature Microbiology), received 25 major awards, and delivered 95 invited/plenary/keynote talks around the world. We are particularly excited by the many collaborations among STROBE members at different nodes, with our 19 industry and 15 national laboratory collaborators, as well as strong joint grant and IP products. Finally, STROBE students and postdocs are in very high demand, with 11 hires into career positions by universities, industry and National Laboratories, mostly within the US.

REPRESENTATIVE STROBE Colorado Publications (STROBE.colorado.edu):

General-purpose, wide field-of-view reflection imaging with a tabletop 13nm light source, C.L. Porter, M. Tanksalvala, M. Gerrity, G. Miley, X. Zhang, C. Bevis, E. Shanblatt, R. Karl, M.M. Murnane, D.E. Adams, H.C. Kapteyn, Optica **4**, 1552 (2017).

Nanoimaging of Electronic Heterogeneity in Bi_2Se_3 and Sb_2Te_3 Nanocrystals, X. Lu, O. Khatib, X. Du, J. Duan, W. Wei, X. Liu, H. Bechtel, F. D'Apuzzo, M. Yan, A. Buyanin, Q. Fu, J. Chen, M. Salmeron, J. Zeng, M. Raschke, P. Jiang, X. Bao, Advanced Electronic Materials, 1700377 (2017).

Sub-wavelength coherent imaging of periodic samples using a 13.5nm tabletop high harmonic light source, D. Gardner, M. Tanksalvala, E. Shanblatt, X. Zhang, B. Galloway, C. Porter, R. Karl, C. Bevis, D. Adams, H. Kapteyn, M. Murnane, G. Mancini, Nature Photonics **11**, 259–263 (2017).

Infrared vibrational nanocrystallography and nanoimaging, E.A. Muller, B. Pollard, H.A. Bechtel, P. van Blerkom, M.B. Raschke, Science Advances **2**, e1601006 - e1601006 (2016).

2/20/18 mm/dc-vb

Appendix C: University of Colorado, Liquid Crystal Materials Research Center

Liquid Crystal Materials Research Center

University of Colorado – Boulder

Total 2017 CHECRA funding $400,000/ Total CHECRA Grant: $400,000 (per year for 6 years)

SUMMARY

The Liquid Crystal Materials Research Center (LCMRC or the Center) has existed on the University of Colorado – Boulder campus since the early 1980s, with block funding from the NSF Division of Materials Research since September 1993. The LCMRC is currently funded as an **NSF Materials Research Science and Engineering Center (MRSEC)**, one of an elite national network of advanced materials research programs.

DESCRIPTION OF THE PROJECT, THE PRINCIPAL PERSONS OR ENTITIES INVOLVED IN THE PROJECT

A major theme of materials science as we enter the 21st century is understanding and manipulation of the interactions between self-organizing complex molecules. It is precisely here that the study of liquid crystals has the greatest impact. Nowhere else are the requirements for understanding the delicate interplay between molecular architecture and its macroscopic manifestations more demanding than in the directed design of liquid crystals.

The Liquid Crystal Materials Research Center is one of the principal centers of liquid crystal study and expertise in the world, its research spanning the range from cutting-edge, basic liquid crystal and soft materials science to the development of enhanced capabilities for commercially important electro-optic, nonlinear-optic, chemical, biological, and other novel applications. The Center is a unique venue worldwide for research on key aspects of liquid crystal science and technology, chief among these the science and application of ferroelectric liquid crystals. The core Center research program is at the University of Colorado, Boulder.

The Center's research is organized within an Interdisciplinary Research Group addressing three major project themes: 1) understanding the relationship between molecular structure and macroscopic materials structure and properties of liquid crystals; (2) inventing new and useful ways of controlling liquid crystal behavior through interaction with surfaces; and (3) inventing and exploring new polymer materials possessing unique properties deriving from liquid crystallinity. Each of these research themes integrates *molecular modeling and design, chemical synthesis, physical studies,* and *applications development* into a multidisciplinary, collaborative research effort.

In 2017, the CHECRA funding was allocated to the three focus areas of the center described in this summary – research, industrial outreach, and education outreach.

FUNDING ALLOCATED TO EACH PRINCIPAL PERSON OR ENTITY

Research - The past year of MRSEC, with NSF funding supplemented by the CHECRA matching state funds, has continued in its role as CU Boulder's single most visible materials research activity nationally and internationally. A summary of major research accomplishments is as follows:

•***Shape-persistent Macrocycle/Nucleobase Hybrids for Assembling Nanostructures*** - A collaboration among CNA IRG2 SIs Zhang, Bowman, Park, and Cha is exploring the properties of small molecule/DNA hybrids (SMDHs) as nanoscale building blocks for engineering 2D and 3D supramolecular DNA assemblies. We have developed an efficient on-bead amide coupling approach to prepare SMDHs with multiple oligodeoxynucleotides (ODNs) strands. Our method is high yielding under mild and user-friendly conditions with various organic substrates and homo- or mixed-sequenced ODNs. Metal catalysts and moisture- and air-free conditions are not required. The products can be easily analyzed by LC-MS with accurate mass resolution. We also explored nanometer sized shape-persistent macrocycles as novel multitopic organic linkers to prepare SMDHs. SMDHs bearing up to six ODNs were successfully prepared through the coupling of aryleneethynylene macrocycles with ODNs, which were used to mediate the assembly of gold nanoparticles. In order to properly characterize the self-assembled nanostructures, conducting photoluminescence, and Raman and Rayleigh scattering spectroscopy on a single nanoparticle or single nanocluster has been employed.

•***Spooling Instability of Self-Propelled Flexible Filament***s – We have been extending our previous work on active matter by developing simulation methods for driven flexible filaments. We are currently applying these methods to study models of motility assays of semiflexible filaments. This project models biophysical experiments in which motors are attached by their tails to a glass surface with their heads sticking into the solution, allowing the motors to attach to and exert forces on cytoskeletal filaments. In a motility assay the motors therefore act as a source of driving, propelling filaments in two dimensions. In early tests of our model, we found that the minimal ingredients of self-propelled, semiflexible filaments which undergo Brownian dynamics and experience steric repulsion with other filaments are able to generate novel nonequilibrium behavior, including the spontaneous formation of filament 'spools': rotating rings of one or more filaments. Filament rings and spools have been observed in motility assays, but a theoretical understanding of their formation and stability is lacking.

•***Two-Dimensional Island Emulsions in Ultrathin, Freely-Suspended Smectic Liquid Crystal Films*** - We have created a novel type of two-dimensional colloidal emulsion, in which arrays of disc-shaped liquid crystal domains are created in ultrathin, freely-suspended, fluid smectic C liquid crystal films. After a film has been drawn across a 25mm diameter aperture, an island emulsion is produced by repeatedly compressing and expanding the film while maintaining vigorous shear and extensional air flow across its area. Once formed, these emulsions restructure over a period of a few minutes to a stable state that then changes only slowly, over the course of several days. This stability enables study of the sedimentation of the emulsion under in-plane gravitation producd by slightly tilting the film, during which the original island emulsion segregates into regions with different kinds of emulsions distinguished by the size, density, and degree of order of the islands. We observe a rich array of phenomena that includes the formation of chains of islands organized into two-dimensional smectics in the dilute phase, and island deformation and coalescence in the condensed phase.

•***Nematic Twist-Bend (TB) Phase*** - The SMRC continues its leadership in the study of the exotic twist-bend nematic phase, currently the most intensely studied by the international LC community. Helical structures in LCs are glide symmetric, i.e. have no electron density modulation, and therefore do not scatter x-rays. In order to study the TB phase we employ the resonant soft x-ray scattering (RSoXS) beamline at the LBL Advanced Light Source, to perform RSOXS at the Carbon Ka edge (x-ray wavelength = 44Å). The RSoXS technique has enabled the first in situ studies of the bulk heliconical nematic structure and pitch as a function of temperature, revealing the dramatic expansion of the TB helix as the higher temperature nematic phase is approached. Recently we have found RSOXS at small angles from the nematic (N) phase above the TB in temperature. Heating in a range of 10°C above the N-TB transition causes this scattering to disappear, identifying its source as orientation fluctuations associated with the impending transition to the TB. This is the first observation of nematic orientation fluctuations by x-ray scattering, opening a powerful new window to the physics of the N-TB transition. We have recently succeeded in developing a simple model of this pretransition behavior which gives an excellent description of the transition. This model couples a helical polarization field representing the intrinsic molecular bend to the average local bend deformation in the phase.

•***New Generation of Clickable Nucleic Acids Exhibit Improved Binding and Specificity to Complementary DNA*** -SMRC researchers have synthesized a second-generation CNA polymer that is one atom shorter compared to the first generation CNA. This challenge required the development of a novel synthetic strategy that will find use in the general preparation of enea-mides, a previously difficult to obtain reactive moiety. These nucleobase monomers react via radical thiol-ene polymerization to furnish oligomers with an internucleobase spacing in line with that of DNA, and as a result, the second generation CNA is capable of binding to DNA in a sequence specific manner. The resulting duplex is stable enough that it can be resolved by polyacrylamide gel electrophoresis. Moreover, a single basepair mismatch greatly diminishes the binding of the polymer, demonstrating that the polymer is exquisitely sensitive to sequence composition. The foremost impact of these results is the development of a synthetic nucleic acid analog that binds to complementary native strands of DNA in low salt and mixed aqueous/organic conditions. This enables the Center to generate materials of higher ordered self-assembled structures that employ the specificity of intermolecular interactions both for their formation and for subsequent function. Furthermore, in contrast to previous protected monomers, these recently developed, acetyl-protected monomers do not inhibit radical reactions, permitting strategies for rapid, sequence specific oligomerization via sequential additions.

•***Rapid Construction of a Step-Growth Polymer with Dynamic Pendant Functionalities*** - In an effort to improve the polymer chain length of CNAs, we have explored the possibility of creating a 'blank slate' polymer onto which pendant functionalities can be later introduced. To this end, we developed the *Scheme* below, a highly efficient, atom-economic, and inexpensive polymerization between divinyl sulfone and *tert*-butylcarbazate, which yields a polymer with more than 60 repeat units, alternating between sulfone and Boc-protected hydrazine moieties. After unveiling the hydrazine functionality, we can install a wide variety pendant groups, including phenyl, furan, pyrrole, pyridine, and nucleobase functionalities, all of which are derived from available aldehydes. Moreover, these pendant groups can undergo dynamic exchange with solution-phase aldehydes, which could enable the rapid construction of polymer-scaffolded dynamic combinatorial libraries.

•***Characterization of Amine-Mediated Retardation of Radical Thiol-Ene Additions*** - Fundamental knowledge of the radical thiol-ene reaction has been generated serendipitously as a result of the CNA research. Amine-mediated retardation of thiol-ene reaction was observed and characterized by the Bowman research group with a mechanistic explanation for the lowered rates. It was determined that addition of thiyl radicals to amine-deprotonated thiols resulted in the generation of relatively stable disulfide radical anions, effectively interrupting the alternating chain transfer, propagation of thiol-ene additions. Various amines, thiols and alkenes were examined and computer simulations performed to validate this mechanism. These results elucidate parameters that may aid chemists achieve successful thiol-ene couplings, designating reactive moieties, substituents or reaction conditions that would be inappropriate. Moreover, as thiol-ene formulations are inherently unstable, this knowledge could lead to strategies for stabilization.

•***Synthesis of Dynamic CNA via Ring Opening Polymerization of Nucleotide Thiolactones*** - SMRC researchers have also created synthetic DNA analogs with dynamic thioester linkages via a novel ring opening thiolactone polymerization. The polymerization efficiency is higher in low polarity solvents with higher molecular weight oligomers observed. The stereochemistry and backbone of the resulting polymer closely resembles that of native DNA as well as that obtained by the ring opening polymerization of nucleobase-modified lactones. In contrast, the thioesters of these resulting polymers, were shown to undergo exchange reactions with free thiols in the presence of a base catalyst. A DNA analog with dynamic covalent bonds in the backbone holds promise for templating reactions in which exchangeable units may rearrange to minimize free energy by binding to their complementary nucleobases.

•***Theranostic Approach Based on Au Nanoparticle and Upconverting Particles Nanostructures Assembled by DNA and CNA*** - Near infrared (NIR) light is an excellent tool for biomedical applications as biological tissues are highly transparent to it and thus produce no background autofluorescence nor unwanted tissue damage. Upconversion nanoparticle (UCNP) emits visible luminenscence under NIR excitation, producing high-contrast images for cellular level detction. Plasmonic nanoparticles such as gold nanorod and nanostar exhibit strong absorption in the NIR region, capable of producing local heating to the point of ablation. By assembling UCNP and Au nanoparticles with DNA and CNA, we have achieved multifunctional nanocluster capable of simultaneously detecting and killing cancer cells. These nanoclusters were then used to breast and bladder cancer cells. Under high intensity NIR laser excitation, substantial cell killing was observed. To further enhance the therapeutic effect, we added a photosensitizer which may be activated by the upconverted visible fluorescence. The dual-mode therapy of photothermal and photodyanmic therapy was found to be the most effective. Finally, to achieve targeted delivery and treatment, we developed a process to conjugate the nanoparticles with antibody to epidermal growth factor receptor and showed selective cell killing was achieved.

•***Molecular Simulations of Polymer Assembly and Gelation using Nucleobase Polymers*** - To understand the thermal stability and structure of hydrogels formed using the physical interactions of CNAs, Jayaraman and team have extended their computational work to show a) how linear and branched polymer (e.g. PEG) conjugation to DNA and click nucleic acid (CNA) strands impact the duplex melting transitions, and b) the assembly and gelation of CNA-polymer conjugates. Using the new coarse-grained model that the Jayaraman's group developed in year 1 of their MRSEC funding [Ghobadi and Jayaraman, Soft matter 12 (8), 2276-2287, 2016], they have shown how conjugating PEG-like polymers (both linear as well as 4 arm stars, impact the melting temperature of the CNA/DNA duplexes as a function of CNA design. For a select few systems, they also confirmed their coarse-grained results with atomistically detailed simulations. These simulation studies published in J Phys Chem B in 2016 [Ghobadi and Jayaraman, J. Phys. Chem. B 120 (36), 9788-9799, 2016] show that small molecular weight polymer conjugation has no significant impact on hybridization of stable CNA duplexes (e.g. high G or C content) but destabilizes weaker CNA duplexes (e.g. high A or T content). Ongoing work is aimed at the assembly of 4-arm polymer conjugated CNA and the thermal stability of these gels/networks as a function of CNA design (sequence, flexibility, presence or absence of charge). Future work will be aimed at understanding solvent effects as well as in understanding how base-base spacing can impact the duplex stability in solution as well as in polymer assembly/network formation.

•***Synthesis and Assembly of Click Nucleic Acid Containing PEG-PLGA Nanoparticles for DNA Delivery*** - delivery of both chemotherapy drugs and siRNA from a single delivery vehicle can have a significant impact on cancer therapy due to the potential for overcoming issues such as drug resistance. However, the inherent chemical differences between charged nucleic acids and hydrophobic drugs have hindered high yield entrapment of both components within a single carrier. We demonstrate here that significant e ncapsulation of nucleic acids is achieved within PLGA containing polymers by incorporating the use of click nucleic acids. First, CNAs were incorporated into a triblock copolymer of poly-(ethylene glycol)-b-CNA-b-lactic-co-glycolic acid (PEG-CNA-PLGA) from which polymer nanoparticles were generated. The CNA-containing polymer particles encapsulated high loadings of DNA complementary to the CNA sequence whereas PEG-PLGA alone showed minimal DNA loading. Furthermore, the dye pyrene could be successfully co-loaded with DNA in the polymer particles as well as a complex, larger DNA sequence that contained an overhang of DNA complementary to the CNA.

•***DNA-Assembled Core-Satellite Upconverting-Metal Organic Framework Nanoparticle Superstructures for Efficient Photodynamic Therapy*** - This work reports the DNA-mediated assembly of core-satellite structures composed of Zr(IV)-based porphyrinic metal-organic framework (MOF) and $NaYF_4$,Yb,Er upconverting nanoparticles (UCNPs) for photodynamic therapy (PDT). MOF nanoparticles (NPs) generate singlet oxygen ($^1O_2$) upon photoirradiation with visible light without the need for additional small molecule, diffusional photosensitizers such as porphyrins. Using DNA as a templating agent, well-defined MOF-UCNP clusters were produced where UCNPs were spatially organized around a centrally located MOF NP. Under NIR irradiation, visible light emitted from the UCNPs was absorbed by the core MOF NP to produce $^1O_2$ at significantly greater amounts than what could be produced from simply mixing UCNPs and MOF NPs. The MOF-UCNP core-satellite superstructures also induced strong cell cytoxicity against cancer cells, which were further enhanced by attaching epidermal growth factor receptor (EGFR) targeting affibodies to the PDT clusters, highlighting their promise as theranostic photodynamic agents.

•***Molecular-scale Photolithography of CNA and Functional groups*** - The goal of this project is molecular-scale light-directed organic synthesis to direct subsequent self-assembly of CNA and DNA on a surface. We first utilize optically written azobenzene monolayers to orient liquid crystal polymers that create a new form of optical mask using the Barry Pancharatnam phase to modulate both the polarization and phase of the optical field. Singularities in this optical field are projected into a flow cell (b) where dark nulls of arbitrarily small size enable top-down patterning of molecular monolayers. Feasibility tests with standard photoresist demonstrate 10-fold violation of the diffraction limit (c). We are now integrating two photosensitive monolayer chemistries into the system including a photolabile cyclooctyne (d) and NPPOC protected nucleobases. We expect in the coming year to demonstrate molecular-scale additive manufacturing of organic species capable of sequence-directed assembly of nano-devices on a solid substrate.

•***Single-molecule nucleic acid sequencing using Quantum Molecular Sequencing (QM-Seq)*** - Nagpal and coworkers, have develop a new single-molecule nucleic acid sequencing method using a high-throughput nanoelectronic method called Quantum Molecular Sequencing. Nanoelectronic DNA sequencing can provide an important alternative to sequencing-by-synthesis by reducing sample preparation time, cost, and complexity as a high-throughput next-generation technique with accurate single-molecule identification. However, sample noise and signature overlap continue to prevent high-resolution and accurate sequencing results, especially for single molecules. Probing the molecular orbitals of chemically distinct DNA nucleobases (Ade nine A, Guanine G, Cytosine C, Thymine T) offers a path for facile sequence identification, but molecular entropy (from nucleotide conformations) makes such identification difficult when relying only on the energies of lowest-unoccupied and highest-occupied molecular orbitals (LUMO and HOMO). Here, nine biophysical parameters were developed to better characterize molecular orbitals of individual nucleobases, intended for single-molecule DNA and other nucleic acids (like CNA) sequencing using quantum tunneling of charges. For this analysis, theoretical models for quantum tunneling were combined with transition voltage spectroscopy to obtain measurable parameters unique to the molecule within an electronic junction. Scanning tunneling spectroscopy was then used to measure these nine biophysical parameters for the different nucleotides in DNA, and a modified machine learning algorithm identified nucleobases. With a mixture of nucleotide measurements used to base call respective DNA nucleobases, it was shown that the new parameters significantly improve base calling ability over merely using LUMO and HOMO frontier orbital energies. Furthermore, at different pH conditions, and hence reversible perturbation of nucleic acid chemistry, extremely high accuracies for identifying DNA bases were observed with a confusion matrix (high true positive and extremely low false positive and negative calls). These results have significant implications for the development of a robust and accurate high-throughput nanoelectronic DNA sequencing technique.

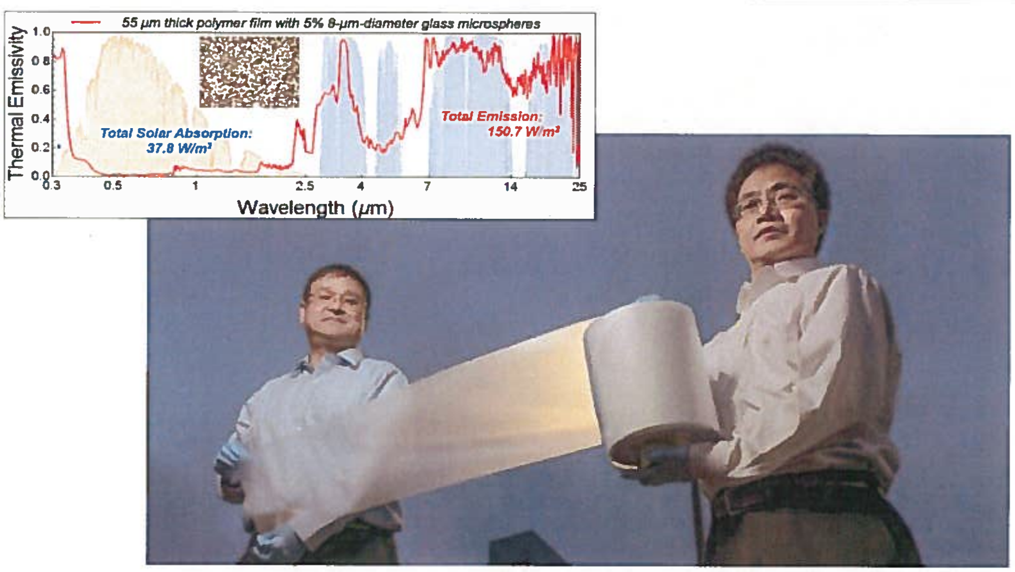

Figure 1: **(inset)** Thermal emissivity vs. wavelength of a polymeric film loaded with glass microspheres. The film is backed with a metal coating that renders it reflective in the visible, and the scattering by the spheres makes it absorbing in the 7 μm to 14 μm range of the atmospheric transmission window, also the peak emission wavelength of room-temperature blackbody radiation. The result is a passive optical metamaterial that on a clear day cools itself by infrared radiation, even in direct sunlight. Xiaobo (left) and Ronggui (right) show a roll of the emissive film of the type recently published in *Science* and made in their labs at UCB.

Industrial Outreach – ***Scalable-manufactured randomized glass-polymer hybrid metamaterial for daytime radiative cooling*** – A glass sphere in a liquid crystal or polymer host Mie scatters and focuses incident light, enhancing the composites's optical absorptivity under appropriate conditions. The Yin group, starting with a Seed Grant from the Center for exploring polymeric metamaterials, and collaborating with the group of Ronggui Yang, found that for glass spheres in polymer hosts this effect can lead to films that are transparent in the visible but strongly absorbing in the infrared (***Figure 1***). If the absorbing wavelength range is the atmospheric transparency window from 7μm to 14μm, such a film near or at room temperature becomes an effective radiator of energy into outer space, capable of cooling itself even in direct sunlight if backed by an effective coating, like silver, that reflects visible light. Demonstrated daylight emissivity is ~ 100 W/m^2, as recently published in Science . This discovery has received international acclaim and commentary in essentially every relevant venue as a result of its promise as an inexpensive way to eliminate waste heat in buildings, cooling systems, and even cars and trucks.

Education Outreach – The Center carries out a variety of education and outreach activities that aim to enhance science literacy and achievement in communities ranging from the general K-12 population to its undergraduate and graduate students. Highlights from the past year are:

•***Materials Science From CU (MSFCU)*** - The Center plans to continue Materials Science from CU, its principal SMRC K-12 outreach activity. This program has been extraordinarily successful in reaching Colorado K-12 students with needed physical sciences presentations tuned for the Colo-rado curriculum. To date over ***2,450*** classes have served ***91,800*** Colorado K-12 students, includ-ing ***120*** classes to ***2,300*** students during this reporting period. These presentations tuned specifi-cally to fit into the Colorado curriculum, provide an excellent way for Center faculty, graduate, and undergraduate students to share their enthusiasm about science with the community.

•***Partnership with Arrupe High School*** – During 2017, the SMRC continued its association with Arrupe. carrying out demonstrations, labs, and science evenings on the topics: introduction to natural and man-made polymers; DNA extraction; gel electrophoresis; and the societal implications of engineering new products.

Diversity – We now have seven current or entering Ph.D. students in UCB graduate STEM programs, who have been recruited through out Cal Poly and Metro State University *Pathways Partnerships.*

2/26/18 nc/dc

Institute for Advanced Composites Manufacturing Innovation (IACMI)
Colorado School of Mines (CSM)
CHECRA Grant: $100,000 (per year for 5 years)
Reporting Period: January 1 - December 31, 2017

Summary:
IACMI's Wind Turbine Technology project focuses on lower the levelized cost of wind energy while simultaneously increasing the quality and reliability of wind turbines. To this end, the project has several targets:

1) Decreasing mold cycle time
2) Integrating thermoplastic matrices into the current production process
3) Augmenting the robustness of fabric placement through automation
4) Conducting in-press nondestructive evaluations (NDE)

The main focus of the team at CSM this past year was to contribute to the first two targets in the project, but advances were also made in the area of NDE (item 4). In CY2017 the CSM team made several key contributions to the goal of the wind technology area. The contributions can be summarized in two main areas:

1) Delivery of a model for the kinetics of free radical polymerization of thermoplastic resins, which can aid in designing the manufacturing processes for wind turbine components. Specifically, it allows one to calculate the exotherms created during the polymerization process for different thickness components (or sections of wind turbine blades). With this knowledge, one can avoid boiling, which creates undesirable defects.
2) Generation of a database of static mechanical properties of the new thermoplastic composites toward certifying their use in the wind industry.

Description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity:

Replacing thermoset with thermoplastic matrices in fiber reinforced composites used to construct wind blades offers the promise of reducing the levelized cost of electricity (LCOE). Thermoplastic use facilitates the end of service life recycling thus providing opportunities to create manufacturing jobs in the conversion of the reclaimed materials. The potential ability of thermoplastics to reduce the manufacturing cycle time strongly affects LCOE and therefore provides the strongest incentive for their commercial adoption. Naturally, for thermoplastic composites to be utilized, the mechanical properties must be equivalent to thermosetting composites.

Principal Senior Investigators	Funding from CHECRA
Aaron Stebner	$100,000

The manner in which each principal person or entity applied the funding in connection with the project

$51,100: Digital image analysis software and measurement equipment was purchased to support the mechanical testing program.

$2,500: Supported 3 undergraduate research assistants to work on the program (~ 265 hrs at $15/hr).

$46,400: Supported administrative assistant Amy Brice and Research Assistant Professor Branden Kappes to assist in facilitating the management of the program and to perform data research on the program.

Results achieved

1. **Mechanical testing of thermoplastic panels**

A vast number of mechanical tests to be conducted on the various resin systems and various fiber layup geometries. In total, 240 individual mechanical tests were conducted for the four fiber layups (*i.e.*, $[0/0/0/0]_2$ from 0 degree, $[0/0/0/0]_2$ from 90 degree, $[0/90/90/0]_2$ from 0 degree, and $[0/90/90/0]_2$ from 45 degree) and three resin systems (*i.e.*, epoxy, Elium® and Nylon-6). Specimens were tested in both tension and compression. The results of this study indicated that the thermoplastic matrices of Elium® and Nylon-6 are suitable for wind turbine blade applications when compared with the mechanical properties of epoxy.

2. **Characterization of fundamental properties of the thermoplastic resin system**

   a) **Characterization and modeling of the exothermic temperature profile of reacting Elium® during the polymerization**

   A valuable, yet simple and inexpensive experiment was designed and implemented to characterize the temperature profile of the Elium® resin during cure. The reaction was conducted in a 25 ml scintillation vial placed in a constant temperature oil bath. The temperature was measured and collected with thermocouples and data logger. In addition, the surface temperature of open bagged VARTM mold as a function of time was recorded using an IR camera. It is critical to keep the temperature of the resin below the boiling point of the monomer during the cure cycle so as not to boil the monomer which causes voids in the composite part. In parallel, a mathematical model was developed by combining reaction kinetics and heat transfer equation. Total of 6 coupled differential equations with 14 parameters and 22 constants are implemented to Wolfram Mathematica®. The heat transfer coefficient and adjustable parameter for initiator efficiency are determined from the experiment. The developed model reasonably capture the induction time and the maximum temperature. The form and parameters for the model have been shared with Purdue University and Convergent (both are IACMI members). They are currently working with implementing the model to their simulation software (RAVEN®).

   b) **Development and utilization of a dual energy X-ray computed tomography scan procedure and a scanning acoustic microscopy procedure for composite void detection**

   Because the existence of voids may significantly reduce their mechanical properties of fiber reinforced composites (FRCs), it is of great importance to characterize and minimize the voids. Especially, in the case of thermoplastic composites via reactive processing, the temperature of resin may locally exceed its boiling point due to the highly exothermic curing reaction. For each of the panels fabricated, a scanning acoustic microscopy image was taken from a representative section of the panel to investigate the presence of voids. Few if any void structures were seen in the images generated from scanning acoustic microscopy. However, another technique was developed for using dual energy X-ray computed tomography (CT) to detect the presence of voids in the composite specimens. Dual energy CT scanning allows much better resolution (sub-micron level) and the distinction between air (voids), polymer (resin), and the glass fibers than that provided by acoustic microscopy or even single energy X-ray CT scans. The results show not only spherical voids in the matrix but also irregularly shaped voids because of the physical contact to fibers. This information can be utilized to optimize the processing conditions and sizing chemistry of the fibers. It is recommended that BP3 plans include examining how the annealing temperature affects the voids sizes and shapes. In addition, future work should include dual energy CT measurements during the mechanical load.

Publications in 2017:

- Suzuki, Y., Cousins, D., Wassgren, J., Kappes, B.B., Dorgan, J., **Stebner, A.P.**"Kinetics and Temperature Evolution during the Bulk Polymerization of Methyl Methacrylate for Vacuum-Assisted Resin Transfer Molding" 2018 *Composites Part A: Applied Science and Manufacturing.*
- Suzuki, Y. Kappes, B.B., Cousins, D. Dorgan, J. Stebner, A.P. "Dual-energy X-ray computed tomography for void detection in fiber-reinforced composites". In Review (submitted November 2017) *Composites Science and Technology.*

Education and Outreach - Partial CHECRA Support

In 2017, the ICAMI project at the school of mines helped support one post-doctoral research associate, two Ph.D. graduate students, three hourly undergraduate students, and two summer undergraduate interns. Workforce development is a cornerstone of the ICAMI mission and the matching funds from CHECRA are critical in this aim.

Summary of benefits to the State of Colorado

- Support of the aforementioned research associates and students who will be highly desirable candidates for Colorado's rapidly growing workforce in the wind energy sector
- Large-scale investment by cost matching from industrial IACMI partners to universities in the state of Colorado
- Exposure of Colorado's intellectual and industrial resources in wind technology to a vast array of industry partners in the IACMI consortia
- Development of the state of the art CoMET facility at the National Wind Technology Center for wind turbine blade research and fabrication
- Ability for local industry and companies to use the School if Mines' extensive background in polymer science and state of the art facilities for mechanical testing

Appendix E

Engineering Research Center Reinvention of the Nation's Urban Water Infrastructure (ReNUWIt)
Colorado School of Mines
CHECRA Grant: $400,000 (per year for 10 years, renewed)
Reporting Period: January 1 - December 31, 2017

Summary: The Engineering Research Center (ERC) for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt) at the Colorado School of Mines, under the leadership of Dr. John E. McCray, is a collaborative effort among four research universities: CSM, Stanford University, University of California at Berkeley, and New Mexico State University. The ERC was established on August 1, 2011 and is the first center to focus on civil infrastructure ever funded by the National Science Foundation.

Cities are facing a mounting water crisis from population expansion, ecosystem demands, climate change, and deteriorating infrastructure that threatens economic development, social welfare, and environmental sustainability. ReNUWIt's vision is to facilitate the transition of existing water supply systems, urban flood control, and wastewater treatment to a new state that will enhance the security and economic vitality of the nation's cities. Accordingly, the goal of this ERC is to advance new strategies for water/wastewater treatment and distribution, develop modular technologies and concepts, and prepare students to lead efforts to reinvent urban water infrastructure.

Description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity

To meet the challenges of reinventing urban water infrastructure, ReNUWIt has three research thrust areas defined as follows:
(1) **Urban Systems Integration and Institutions:** Support the reinvention and restoration of urban water systems through the development of decision-making tools that enable sound decision making about future investments in urban water infrastructure;
(2) **Efficient Engineered Water Systems:** Develop new, modular technologies to overcome barriers that prevent wider application of existing by underutilized technologies and collecting data on technical performance;
(3) **Natural Water Infrastructure Systems:** Develop technologies for managing natural systems to treat and store water while simultaneously improving urban aesthetics, with focus areas in stormwater treatment for beneficial use and groundwater recharge.

Water resource planners are hesitant to integrate new types of engineered treatment systems into their water portfolio due to uncertainties about cost, reliability, public health risks, and overall impacts on system performance. Thus, a mechanism for technology assessment is needed at scales ranging from the laboratory to the full-scale service area. Such capabilities do not exist and as a result, many good ideas are not brought into practice. To facilitate the integration of new technologies into urban water systems, tools like life-cycle assessment for decision-making are being advanced as well as conducting research and implementation of engineered systems. The strategic research plan continues to evolve in response to research outcomes, supplemental funding opportunities, and new information related to achieving ReNUWIt's overarching goals.

Appendix E

Within the *Urban Systems Integration and Institutions* thrust, research focuses on the development of integrated regional water models. The goals of the thrust area are to: (i) develop integrated decision support systems for utility planning; (ii) develop integrated visioning, assessment, and implementation tools for regional and municipal water planning; and (iii) identifying "technology diffusion pathways" to increase the likelihood of technology implementation. Mines is examining the legal, economic and technical feasibility of beneficial use of stormwater in a redeveloping neighborhood in northwest Denver (Berkeley neighborhood) including a method to project increases in impervious areas and the subsequent impact to stormwater flows and quality.

The goal of the *Efficient Engineered Systems* research thrust is to characterize the viability of existing but underutilized technologies at different scales by assessing their economic, environmental, and social costs and benefits. The specific aims of this thrust are: (i) develop improvements to energy and resource recovery from existing municipal wastewater systems; (ii) develop or asses new processes, approaches, and practices that support direct potable reuse of municipal wastewater; and (iii) advance (i) and (ii) to pilot-scale and full-scale demonstration and adoption. Research at Mines has incorporated smart system controls to monitor/ model/ optimize the hybrid sequencing batch-membrane bioreactor (SB-MBR) system operation for nutrient management (e.g., tailored water management).

The thrust area on the use of *Natural Water Infrastructure Systems* brings a much-needed quantitative approach to an area that has not previously been subjected to rigorous engineering analysis. The realigned goals of the thrust area are to: (i) develop novel approaches for manipulating subsurface natural system unit processes to predictably enhance stormwater and treated wastewater qualities; (ii) identify new ways of designing and operating unit process to maximize water quality and flood protection while enhancing function and aesthetics; and (iii) deploying sensors and actuators for real-time control and management of processes. Research at Mines is advancing passive treatment of stormwater through bioinfiltration systems and the hyporheic zone in streams.

Within the ReNUWIt framework described above, twelve projects were funded in 2017:

- Innovative Stormwater Management in Denver (U2.5);
- Sustainable landscape irrigation with reclaimed water (E1.5);
- Microalgae for wastewater treatment and recovery: A new approach to onsite wastewater treatment (E2.2);
- Reclaiming Energy from Wastewater using Anaerboic Digestion (E2.4);
- Tailoring Water Reclamation for Specific Purposes (E2.9, formerly E1.1);
- Chemical valorization of Energy from Waste (E2.12);
- Phosphorus Recovery in Existing Wastewater Treatment Facility Infrastructure (E2.16, new project 2017);
- Alternative Potable Reuse Treatment Trains (E3.4);
- Smart Engineered Wetlands (N1.2);
- High Resolution Urban Stormwater Modeling (N3.1);
- Stormwater Infrastructure for Water Quality (N3.3); and
- Engineering Streambeds for Water Quality Improvement (N3.4).

Appendix E

Principal Investigators	Funding from CHECRA
John McCray, CSM Principal Investigator Center Lead Project co-Lead, Innovative Stormwater Management in Denver, U2.5 Project Lead, Engineering Streambeds for Water Quality Improvement, N.3.4	 $6,074 $31,818 $750
Tzahi Cath Project Lead, Tailoring Water Reclamation for Specific Purposes, E2.9	 $7,758
Linda Figueroa Project Lead, Reclaiming Energy from Wastewater using Anaerboic Digestion, E2.4 Project Lead, Novel phosphorus extraction/recovery schemes and implementation within existing wastewater treatment facility infrastructure, E2.16	 $3,098 $8,502
Christopher Higgins Project Lead, Stormwater Infrastructure for Water Quality, N3.3 Project co-Lead, Engineering Streambeds for Water Quality Improvement, N.3.4	 $5,394
Terri Hogue Project co-Lead, Innovative Stormwater Management in Denver, U2.5	 $31,818
Reed Maxwell Project Lead, High Resolution Urban Stormwater Modeling, N3.1	 $12,036
Jonathan Sharp Project Lead, Smart Engineered Wetlands, N1.2	 $7,462
TOTAL SPENDING (Jan-Dec 2017)	***$114,710***

Within the ReNUWIt projects (2017), full or partial support was provided to:

- 11 Doctoral students
- 4 Master's of Science Thesis students
- 12 Hourly Undergraduate students
- 3 REUs ~ a 10 week summer program designed to provide research experience for undergraduates
- 1 Post Doctoral Fellow
- 3 Assistant Research Faculty
- 4 Research Staff
- 1 Teaching Assistant Professor
- 10 Faculty ~ 1 Assistant Professor; 3 Associate Professors; and 6 Professors

The manner in which each principal person applied the CHECRA funding in connection with project results

John McCray, Professor: Discretionary center funding for supporting new research directions. In support of the Denver Stormwater Planning project (U2.5) CHECRA funding supported tuition, stipend and nominal materials for one PhD student, and two undergraduate students to assist with frameworks to overcome policy and legal barriers to allow stormwater beneficial use and one teaching faculty for data synthesis in development of engineering drawing at Willis Case Golf Course. As an outcome of this work, the City of Denver has changed the policy on how redevelopment on lots <1 acre are permitted. A method developed previously to estimate increased development and increased impervious area due to infill development this west

Appendix E

Denver neighborhood has been adopted by the City and County of Denver for application across the entire city. M.S. student Lisa Cherry, who developed the method as part of her M.S. Thesis, is now working in the Planning department for the City and County of Denver.

Nominal materials were supported for field scale testing and implementation of engineered urban streambeds for water quality enhancement thru BEST (N3.4; note, one PhD graduate student was supported with NSF funds). As an outcome of this work, Dr. McCray secured a partnership with the City of Golden, to engineer streambeds in stormwater channels to improve water quality. Mines and Golden are jointly working on Proof of Concept (POC) Innovation grant, awarded by an external technical advisory board of Colorado business entrepreneurs. Urban Drainage and Flood Control is also looking for an opportunity to test the BEST system for stormwater quality improvement.

Tzahi Cath, Associate Professor: Funding for one graduate student focused on SB-MBR energy optimization and tailored non-potable reuse of treated wastewater (E1.1). This research is leveraged with a PhD graduate student supported by NSF funds.

Linda Figueroa, Professor: Funding provided support for two undergraduate students to sample and analyze the pilot scale anaerobic bioreactor at Plum Creek Wastewater Authority (E2.4). Leveraged with this work is a Lieutenant Colonel in the US Army working on his PhD as part of the US Army's Advanced Civil School program. Upon graduation from Mines he will be an Assistant Professor at the U.S. Military Academy at West Point teaching and conducting research in environmental biotechnology and microbiology studies. Outcomes from this work have transformational changed in the current wastewater treatment paradigm. In addition, CHECRA funds supported tuition for two graduate students and hourly support for two undergraduate students working on phosphorus recovery within existing wastewater treatment facility infrastructure (E2.16, new project start in 2017). Both graduate students are currently employed with Metro Wastewater Reclamation District and are expected to directly implement research findings at the District.

Christopher Higgins, Associate Professor: Partial support for one post doctoral fellow for work with the City of Denver to develop of a field site at Cuernavaca Park and with the City of Golden for pilot scale testing of BioCHARGE (N3.3). BioCHARGE is designed to treat stormwater pollutants, particularly pathogens, but also organics and metals via infiltration through innovative engineered geomedia.

Terri Hogue, Professor: One undergraduate student was supported for hydrologic modeling of the Berkeley neighborhood in northwest Denver and partial salary support for Dr. Hogue for student oversight (U2.5). A goal of this work was to evaluate the potential for additional stormwater runoff generated due to increased infill development to help meet future water demands via non-potable use. Nominal funds were provided for stormwater quality analyses and supplies.

Reed Maxwell, Professor: One graduate student was supported looking at stormwater flow and quantity impacts of converting pervious areas to low impact development in urbanized watersheds (N3.1). Specifically modeling has evaluated the impacts associated with converting 15%, 25%, 35% and 50% of existing pervious areas under different design storms (2-Yr, 5-Yr, 10-Yr, 50-Yr, 100-Yr) on flooding.

Jonathan Sharp, Associate Professor: Partial faculty salary support was provided for student and research faculty advising and mentoring (N1.2) for engineering smart wetlands designed to remove specific pollutants of interest. Nominal salary support was provided to one research assistant professor to evaluate attenuation of trace organic chemicals in managed aquifer recharge systems (N2.2).

Results Achieved

Results from the *Urban Systems Integration and Institutions* thrust continued to focus on stormwater planning, management and treatment. In partnership with the City and County of Denver (U2.5), feasibility analysis and conceptual design for beneficial use of non-potable stormwater in the Denver Berkeley neighborhood using regional best management practices (BMPs) is continuing. Implementation at parks and recreation land would enable potential urban irrigation while meeting water quality standards for discharge into Clear Creek, and stakeholder regulatory and sustainability goals. In 2017, installation of a stormflow and water quality monitoring network was completed. The methodology developed by ReNUWIt to predict future land-use and impervious area changes for urban infill redevelopment is being expanded by the City of Denver to predict infil development and impervious areas city-wide. Finally, hydrologic modeling to estimate and predict increased stormwater runoff due to multiple infill development scenarios continued.

Results from the *Efficient Engineered Systems* research thrust continued to rely on field research on the Mines campus utilizing sequencing batch membrane bioreactor treatment of wastewater from housing at Mines (~7,000 gal/day). The demonstration-scale treatment unit allows effluent qualities to be tailored to various reuse applications (i.e., urban landscape irrigation; streamflow augmentation; groundwater recharge) and continues to be supported through collaborations with manufacturers and start-up companies within Colorado. Identifying mechanisms (E2.9) by which nutrient removal can efficiently be achieved while lowering energy consumption is beneficial both from an energy resource standpoint and an economic perspective. Alternatively, E2.9 also investigates strategies for optimization of generating on-demand effluent qualities with elevated levels of nitrogen while simultaneously optimizing energy demands continue. A fifth season of fertigation (use of reclaimed wastewater for irrigation to optimize nutrient removal and application) was completed with analyses of leachate, and soil samples collection to assess using tailored water to reduce potable use and mineral fertilizers, and minimize nitrate leaching to groundwater (E1.5).

Demonstration scale Coupled Hybrid Anaerobic Reactors for Generation of Energy (CHARGE) have been operating at the Plume Creek Water Reclamation Authority (PCWRA) in Castle Rock for five years to evaluate the long-term viability of generating energy from wastewater. The project involves operations considerations such that small utilities can make use of an anaerobic treatment process to generate methane that can be used for energy while eliminating the need for aeration. The results from primary anaerobic treatment have led to additional investment by NSF ($329K; Sept 2015 – Aug 2018) and Water Environment Research Foundation (106K; May 2016 – Apr 2019) to enhance our understanding of the fundamental processes in a pilot system with primary and secondary anaerobic treatment stages constructed and operated at the Mines Park Test Bed Facility. Future efforts will focus on converting the anaerobic reactors at PCWRA to trailer mounted units that can be mobilized to various locations where wastewater is generated. Discussions with MillerCoors in Golden, and Littleton Englewood WWTP have explored piloting CHARGE. Littleton Englewood WWTP is expected to pilot CHARGE in 2018-2019.

Appendix E

A project to evaluate phosphorus extraction/recovery schemes and pilot scale implementation within existing wastewater treatment facility infrastructure was started in 2017 (E2.16). Metro Wastewater Reclamation District (District) is currently undergoing extensive upgrades to the Robert W. Hite Facility (RWHTF) to meet increasingly stringent nutrient regulations, particularly focused on effluent discharge phosphorus concentrations. Enhanced biological phosphorus removal (EBPR) is a sustainable and cost effective means to remove phosphorus from the liquid stream, however the process has been shown to negatively impact other process areas in both performance and cost. As a result, the District has continued developing near-term and potential long-term phosphorus management options, harnessing the experience of industry leaders and university expertise to make informed infrastructure and operating strategy decisions that best serve the 1.8 million Denver Metro area ratepayers. This project research will evaluate EBPR for improvements and optimization to maintain low effluent phosphorus concentrations while improving the effectiveness and efficiency of the RWHTF in other areas.

Results from the *Natural Water Infrastructure Systems* thrust continued to focus on developing smarter, more efficient methods for infiltrating recycled water for aquifer storage while simultaneously improving water quality. These sustainable technologies capitalize on the management of natural treatment processes to facilitate water treatment while enhancing storage infrastructure. For example, upscaling for field testing at the field scale of modules termed "Biohydrochemical Stream Water Treatment (BEST)" continued (N3.4). Development and implementation of new geomedia (BioCHARGE) through field scale testing in collaboration with the City of Denver at Cuernavaca Park and the City of Golden for removal of stormwater pollutants during infiltration also continued (N3.3). An outcome from this work was the successful DoD SERDP award ($491K; 2018 - 2020) to improve BMP stormwater treatment designs to prevent sediment recontamination. Several staff members on this new project work for Geosyntec, based in Colorado, further increasing the technical and financial impact to the State. In another leveraged project, we are also working with the USGS National Water Quality Lab, evaluating sources of organic chemicals in urban stormwater, BMPs for removal from urban stormwater, and redesign of bioinfiltration systems to control both the quantity and quality of urban stormwater in Colorado.

Stormwater modeling (N3.1) simulations within the South Platte River Basin, southeast of Downtown Denver in Parker provide ultra-high-resolution (1 m extent) detail on water movement on the surface (i.e. routing water from the rooftop to the gutters and into the drains) and subsurface (i.e. routing water through complex layers of biofilters or within BMPs) providing information to municipalities on how design, placement, and material usage of stormwater infrastructure impacts in-situ water quality and peak storm flow mitigation.

Research continued to develop novel types of unit process wetlands (N1.2) capable of remediating a diverse suite of water contaminants. Through this work, improved understanding of the mechanisms through which nutrients and trace organic contaminants are removed which can be used to design, operate and maintain more cost effective and reliable wetland treatment systems has been gained. An outcome of this work and the wetland constructed in Southern California is an active collaboration with the USGS Colorado State office in Boulder, CO to investigate the broader applicability of this type of wetland system to other regions.

Appendix E

Summary of Benefits to the State of Colorado

- Received \$830,000 NSF core funds in 2017. These funds in combination with CHECRA funds (\$400,000) and \$115,000 CSM matching funds have supported:
  - 33 graduate students (tuition and stipend) in the first 6.5 years of ReNUWIt (2011-2017) with degrees in Civil & Environmental Engineering, Hydrologic Science and Engineering. Women comprised ~40% of these graduate students. Many of these students are expected to enter or remain in the Colorado STEM workforce.
    - December 2017 MS graduate is now employed at Littleton Englewood WWTP.
    - Two existing graduate students are employed by Metro Wastewater Reclamation District
  - Research experiences for 32 Mines undergraduates with ~50% of these students female.
- Continued collaboration with the City and County of Denver, the Urban Drainage and Flood Control District (UDFCD), and Enginuity Engineering Solutions, to evaluate how low impervious design (LID) impacts on urban flooding using high resolution models. Methodology developed to predict future land-use and impervious area changes for urban infill redevelopment is being used by the City of Denver to predict infil development and impervious area city-wide.
- Collaboration with Metro Wastewater Reclamation District and Carollo Engineers investigating potential energy savings and treatment efficiencies associated with alterations in treatment plant operation for nutrient removal. Successful improvements lower energy consumption and subsequent application of reclaimed wastewater to fertigation decreases the level of nutrient removal required.
- A biohydrochemical enhancements for streamwater treatment (aka, BEST) pilot channel has been constructed with support from the City of Golden. In addition, Seattle Public Utilities provided \$50k for installation recommendations for BEST stream restoration and floodplain reconnection tentatively planned for 2019.
- Successful pilot scale testing of anaerobic treatment process to generate energy at the Plum Creek Water Reclamation Authority has led to plans for expanding piloting at Littleton Englewood WWTP.
- Demonstration that algal wastewater treatment systems can be combined with biorefinery operations to realize net positive energy treatment of domestic wastewater throughout the year in different seasons representative of Colorado.
- Identification of a variety of economically viable products, including liquid and gaseous fuels and nitrogen and phosphorus fertilizers, that can be recovered from wastewater treatment systems via integrated bio-hydrothermal-electrochemical technologies being developed in Colorado.
- Continued collaboration with researchers at NREL pioneering an innovative approach to producing gasoline from wastewater through an integrated biological and thermochemical processing platform that can serve as the basis for replacement of petroleum resources.
- Continued success obtaining new researcg grants at Mines with Colorado collaborators (USGS, Geosyntec) to broaden the design and implementation of ReNUWIt developed treatment systems and approaches. These grants will support graduate and undergraduate students, many of which are expected to enter or remain in the Colorado workforce.
- Bi-monthly seminars organized and sponsored by the ReNUWIt students. Seminar speakers and topics include a range of student research, industry partners, and experts.

Appendix E

Publications in 2017 (funded wholly or in part with CHECRA funds):

<u>Thesis and Dissertations:</u>

Fry, Timothy (2017). High Resolution Modeling for Water Quantity and Quality, Understanding the Role of Green Infrastructure Best Management Practices in Ultra Urban Environments: Connections, Feedbacks, and Interactions. PhD. Dissertation. Hydrological Science & Engineering, Colorado School of Mines, Golden, CO. (funded wholly with CHECRA funds)

Herzog, Skuyler (2017). Biohydrochemical Enhancements for Streamwater Treatment: Engineered Hyporheic Zones to Increase Hyporheic Exchange, Control Residence Times, and Improve Water Quality. PhD. Dissertation. Hydrological Science & Engineering, Colorado School of Mines, Golden, CO.

Jones, Zack (2017). Microbial Ecology and Functional Insights into Contaminant Bioattenuation in Engineered Shallow Open Water Treatment Wetlands. PhD. Dissertation. Civil and Environmental Engineering, Colorado School of Mines, Golden, CO.

Ramey, Dotti (2107). The Implications of Tailored Water Treatment in Distributed Wastewater Reclamation: Investigation of Biological Stability and Energy and Nutrient Recovery. PhD. Dissertation. Civil and Environmental Engineering, Colorado School of Mines, Golden, CO.

<u>Publications:</u>

LeFevre, G.H., Lipsky, A., Hyland, K.C., Blaine., A.C., Higgins, C.P., and R.G. Luthy (2017). Benzotriazole (BT) and BT Plant Metabolites in Crops Irrigated with Recycled Water. *Environmental Science: Water Research & Technology.* 3: 213-223.

Li, Y., S. Leow, A.C. Fedders, B.K. Sharma, J.S. Guest, and T.J. Strathmann (2017). Quantitative Multiphase Model for Hydrothermal Liquefaction of Algal Biomass. *Green Chemistry.* 19: 1163-1174.

Li, Y., S.A. Slouka, S.M. Henkanatte-Gedera, N. Nirmalakhandan, T.J. Strathmann (2018). Demonstration and Evaluation of an Integrated Algal Wastewater Treatment and Valorization System. *In review with Water Research.*

Jones, Z.L., J.T. Jasper, D.L. Sedlak, and J.O. Sharp (2017). Sulfide-Induced Dissimilatory Nitrate Reduction to Ammonium Supports Anammox in an Open-Water Unit Process Wetland. *Applied and Environmental Microbiology*, 00782-17

Jones, Z.L,. K. Mikkelson, M.T. Nygren, D.L. Sedlak, and J.O. Sharp (2018). Establishment and Convergence of the Photosynthetic Microbial Biomats in Shallow Unit Process Open-Water Wetlands. In press. *Water Research*

Panos, C., T.S. Hogue, R. Gilliom, and J.E. McCray (2018). High-resolution Modeling of Infill Development Impact on Stormwater Dynamics in Denver, Colorado. *Journal of Sustainable Water in the Built Environment*. Accepted with revisions.

Pfluger A., J. Callahan, J. Stokes, D. Ramey, L. Figueroa and J. Munakata Marr (2018). Energy Positive Wastewater Treatment: Life-cycle Analysis of Mainstream Anaerobic Treatment of Domestic Wastewater, *In review with Environmental Science and Technology.*

Pfluger A., J. Starke, S. Cosper, J. Munakata Marr and L. Figueroa (2018). Biogas Generation from Waste: Overcoming Barriers to Widespread Implementation of Anaerobic Technologies in DoD for Energy Security. I*n review with The Military Engineer.*

Ulrich, B.A., Loehnert, M. and C.P. Higgins (2017). Improved contaminant removal in vegetated

stormwater biofilters amended with biochar. *Environmental Science: Water Research and Technology*, 3: 726-734.

Ulrich, B.A., Vignola, M., Edgehouse, K., Werner, D., and C.P. Higgins (2017). Organic carbon amendments for enhanced biological attenuation of trace organic contaminants in biochar-amended stormwater biofilters. *Environmental Science and Technology*, 51(16): 9184-9191.

Appendix F

Advanced Thin Film Photovoltaics for Sustainable Energy

Matching Funds for NSF AIR:RA Award: 9/1/2015 to 8/31/2018
Colorado State University
CHECRA Grant ($400K for 3 years)
Annual Report; February 19, 2018

Summary: This Accelerating Innovation Research (AIR) project is advancing both the development of higher-efficiency CdTe-based photovoltaic (PV) devices and their timely integration into large-scale manufacturing. The project is the basis of a research alliance that includes the Next Generation Photovoltaics Center (NSF I/UCRC) at Colorado State University (CSU), the National Renewable Energy Laboratory, the Center for Renewable Energy Systems in UK (CREST), and the First Solar, Advanced Solar Power, and 5N Plus companies. The past year has been highly productive in terms of research results and publications, student training and employment, and impact on Colorado.

1. Description of the project, the principal persons and the amount of funding

1a. CdTe Photovoltaics for Sustainable Energy: Energy sustainability is one of the grand challenges facing modern society, and CdTe thin-film solar PV provides a proven opportunity for rapidly expanding renewable energy. CdTe PV is currently competitive for generating electricity in much of the world and providing electricity at 6 US cents/kWh and below from utility scale projects without subsidy. Recently an agreement was made to sell electricity from CdTe PV from a new 100 MW field at 3.87 US cents/kWh [http://www.bloomberg.com/news/articles/2015-07-07)]. Total CdTe installations are now over 18 GW, and annual production is likely to double in the next two years. The goal of the project is make CdTe still more cost effective with additional advances. In the past year, it has advanced CSU's state-of-the-art deposition systems and has pursued two separate routes to higher-efficiency manufacturing-friendly cells: (1) the inclusion of CdTe alloys at the front and back of the cells for improved single-junction structures, and (2) the development of PV devices with higher band gaps for multi-junction cells. The roadmap for the Center's PV program is shown in Fig. 1 below:

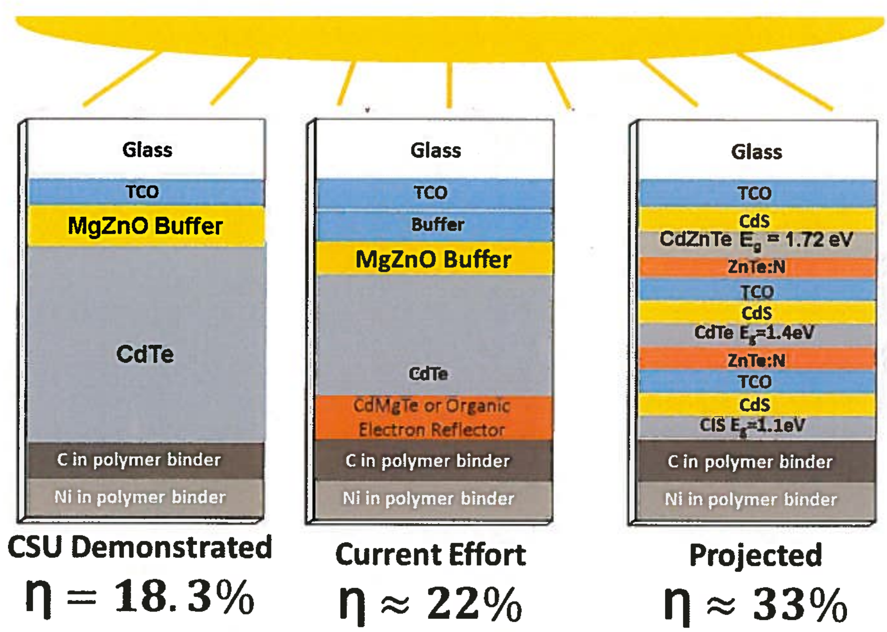

Figure 1: Efficiency Roadmap for CdTe Photovoltaics at CSU.

1b. Funding from CHECRA and allocation: The PI for this project is Prof. W. S. Sampath and the Co-PIs are Prof. J. R. Sites and K. L. Barth. The Co-PIs jointly allocate the funding ($400K for 3 years) from CHECRA. During the past year, CHECRA funds have been used for at partial support of Research Scientist Jason Kepart, Research Associate Jennifer Drayton, Laboratory Engineer Kevan Cameron, and for support of the students working on the project (see Section 3).

2. Results Achieved February 2017 through January 2018

The advanced co-sublimation vapor source (first project goal) that was fabricated at CSU for the deposition of CdMgTe and CdZnTe alloys is shown in Fig. 2. This two-chamber source has been in productive use during the past year for deposition of the higher band-gap materials for the top cell in tandem structures such as shown in the right-hand panel in Fig. 1. The upper chamber contains the CdTe source material, and the lower one the Mg or Zn to form the alloy. Each chamber has a precision-controlled shutter, which allows control of the alloy composition and can form a well-defined graded layer when desired. This capability is unique and not available elsewhere. As with the other components of the deposition system, the operation is fully programmed and recorded. Of particular note, the source was designed internally at CSU and assembled and maintained by the research team with assistance from the Golden branch of Anderson Dahlen's Applied Vacuum Division and Quantum Clean in Colorado Springs.

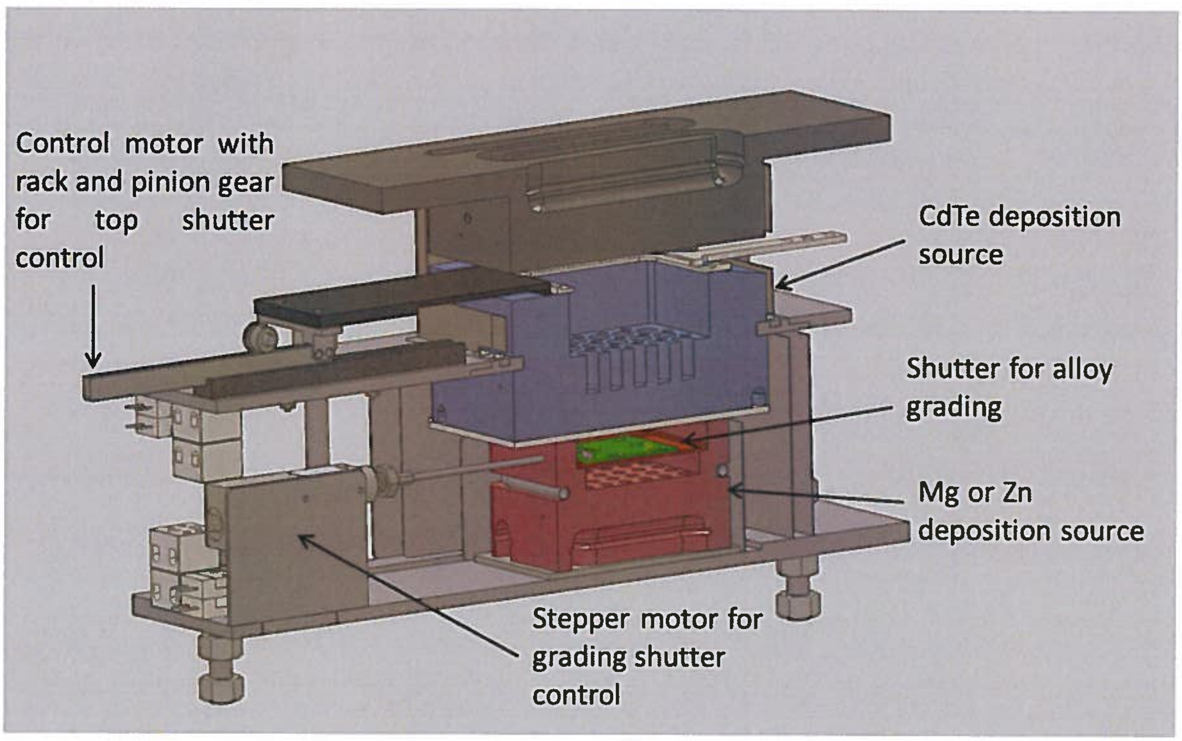

Figure 2. Two chamber co-sublimation source for alloy deposition.

Examples of compositional control with the co-sublimation source are shown in Fig. 3. The left panel shows the band-gap of CdZnTe, and the right shows a series of CdMgTe optical transmission curves that determine its band gap, where the fraction of Zn or Mg was systematically varied. With both alloys, the variation in band gap covers a wide range and can be accurately programmed. The project has now demonstrated that CdMgTe with an appropriate capping layer and passivation process produces an effective electron reflector (second project goal) and that CdZnTe with a band gap of 1.7 eV produces cells with respectable efficiency and quantum efficiency greater than 70% (third project goal).

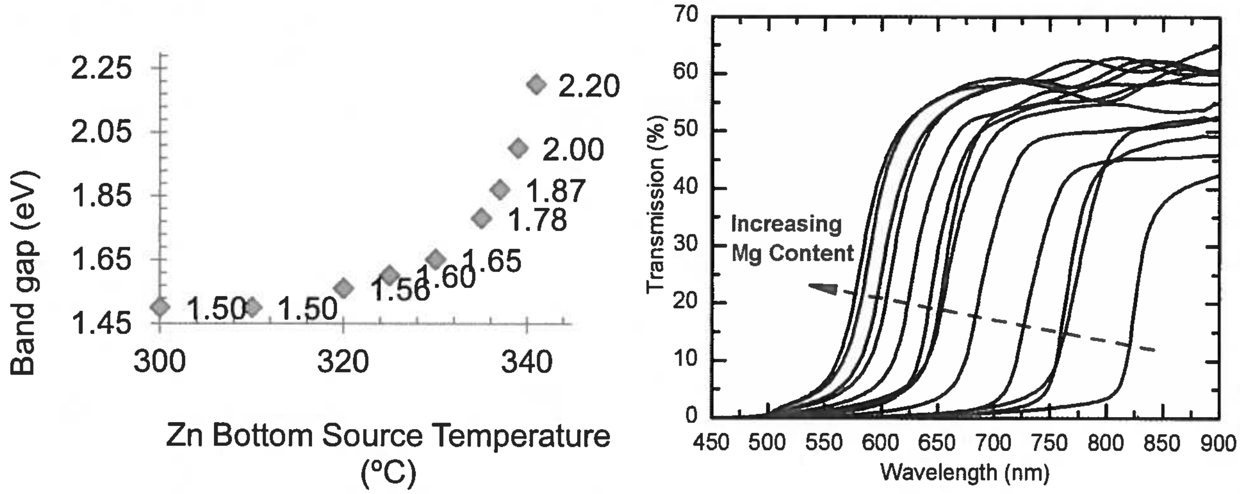

Figure 3. Ability of the co-sublimation source to control the composition and band gap of CdZnTe (left) and CdMgTe (right).

The fourth project goal has been to expand the measurement and analysis capabilities of the team. Of direct relevance to the project has been microscopy and photoluminescence work done with the partners at NREL and Loughborough respectively. At the same time the team has made improvements to absorber passivation with $CdCl_2$ and to cell contacting through the use of Te and Mg(O,N) layers.

3. Additional Benefits to Colorado: Student Training

Student training and introduction to the workforce is a central part of the CHECRA-supported project. The PV group has a strong team approach to this training. It brings in outside speakers, particularly those involved in industrial research and development, it has an effective mentoring program where the more senior members work closely with the newer ones, and it meets as a group each Friday for presentations on a rotating basis by the students and other group members.

Several undergraduate and graduate students, including a visiting student from Loughborough, have been key parts of the project's success during the past year. Two of the undergraduates (Christina Moffett and Carey Reich) completed their B.S. degrees and are continuing towards their M.S. At the graduate level, four students completed their Ph.D.:

Drew Swanson, now at Broadcom, Fort Collins, CO
Amit Munshi, now at Research Scientist at CSU
Tao Song, now at the National Renewable Energy Laboratory, Golden, CO
Andrew Moore, now at Intel, Portland, OR

and two postdoctoral team members have also moved to industrial positions in 2017:

John Raguse, Broadcom, Fort Collins, CO
Jason Kephart, First Solar, Santa Clara, CA

Publications in Past Year

1. T.M. Shimpi, J. Drayton, D.E. Swanson, and W.S. Sampath, "Properties of nitrogen-doped zinc telluride films for back contact to CdTe photovoltaics, *J. Electronic Materials* **46**, 5112-5120 (2017).

2. D. E. Swanson, J.R. Sites, and W.S. Sampath, "Co-sublimation of $CdSe_xTe_{1-x}$ Layers for CdTe Solar Cells," *Solar Energy Mat. and Solar Cells* **159**, 389-394 (2017).
3. T. Song, A.M. Moore, and J.R. Sites, "Te Layer to Reduce the CdTe Back Contact Barrier," *J. Photovoltaics* **8**, 293-298 (2018).
4. A. Munshi, J. Kephart, A. Abbas, J. Raguse, J.-N. Beaudry, K. Barth, J. Sites, J. Walls, and W. Sampath, "Polycrystalline CdSeTe/CdTe graded-absorber cells with 28 mA/cm^2 short-circuit current," *J. Photovoltaics* **8**, 310-314 (2018).
5. M. Amarasinghe, E. Colegrove, H. Moutinho, D. Albin, J. Duenow, S. Jensen, J. Kephart, W. Sampath, M. Al-Jassim, S. Sivanathan, and W. Metzger, "Increasing CdTe grain size and carrier lifetime on CdSe, MZO, or CdS," submitted to *J. Photovoltaics*.

Conference Proceedings

1. J.M. Kephart, A. Kindvall, D.D. Williams, D. Kuciauskas, P. Dippo, and W.S. Sampath, "Sputter deposited oxides for front-contact passivation of CdTe photovoltaics," 44th IEEE Photovoltaics Specialist Conference, Washington DC, June 2017.
2. A. Munshi, P. Kaminski, A. Abbas, S. Chinna, S. Chandralal, J. Walls, and W. Sampath, "Characterization of CdTe photovoltaic devices passivated using hydrogen plasma," 44th IEEE Photovoltaics Specialist Conference, Washington DC, June 2017.
3. T. Song and J.R. Sites, "Role of tellurium buffer layer on CdTe solar cells' absorber/back-contact interface," 44th IEEE Photovoltaics Specialist Conference, Washington DC, June 2017.
4. A Kindvall, J.M. Kephart, J.A. Drayton, J.D. Williams, and D.D. Williams, "Molybdenum oxide and molybdenum nitride back contacts for thin-film CdTe solar cells," 44th IEEE Photovoltaics Specialist Conference, Washington DC, June 2017.

Major Presentations

1. Amit Munshi, "Polycrystalline CdSeTe/CdTe graded-absorber cells with 28 mA/cm^2 short-circuit current," 44th IEEE Photovoltaics Specialist Conference, Washington DC, June 2017, received Best Student Presentation award.
2. James Sites, "Enhancements to CdTe cell efficiency", 33rd European Union Photovoltaic Science and Engineering Conference, Amsterdam, Sept 2017. Plenary presentation.

Appendix G

Root genetics in the field to understand drought adaptation and carbon sequestration

ARPA-E ROOTS Award
Colorado State University
CHECRA Grant ($325.6K over 3 years)

Summary: We propose to develop a high-throughput phenotyping platform to measure root system traits, soil carbon and nutrients, as well as mapping soil surface greenhouse gases (GHG). This platform will be used in field experiments to identify genetic variation in root traits and their effect on soil C stocks and GHG. This understanding will then be used to improve root trait-based model predictions of soil GHG emissions and soil carbon sequestration to depth in an integrated project advancing both trait development and field screening. The project started on 3 July 2017.

Description of the project, the principal persons and the amount of funding:
We will utilize a diverse set of maize lines to examine for root structure and composition under full and limited irrigation in Colorado and Arizona. They will be phenotyped with our existing approaches as well as newly developed root (root pulling force) and soil (Dopper Raman spectroscopy) HTP approaches. The understanding derived from these experiments and the data on root and soil response variables will be used to develop and evaluate a new generation process-based model, to be used to enhance translation and improve throughput of breeding as well as a tool to quantify the impacts of root parameters across ideotypes on soil C sequestration and GHG emissions in different environments. For category 2 we will develop novel sensors, incorporating them into our already functioning field HTP systems. The most promising methods and sensors will be used to identify genomic regions that influence root and soil traits and their sensitivity to drought by screening large mapping populations in the field. Data from this larger field effort will be used to validate the new model. The principal persons involved at Colorado State University are PI John McKay, as well as Co-PIs Randy Bartels, Thomas Borch, Francesca Cortufo, and Keith Paustian.

Funding from CHECRA and allocation:
The CHECRA funds have been used to support PI John McKay, Research Scientist Jack Mullen, research associate Anne Howard, as well as a soon-to-be-hired overall project manager. The CHECRA funds have also enabled purchase of a EarthSense TerraSentia high-throughput phenotyping robot as part to enhance our field measurement capabilities.

Results Achieved:
RPF sensor testing platform assembly
In order to test the RPF sensor in the field, Czero has designed a mobile testing platform. This platform is designed to transport the RPF sensor to a planted field and support the sensor during testing. Design specifics for this platform were outlined previously. Manufacture and assembly of this platform was started in Q2. All custom and COTS parts have been received and testing of individual components has begun. The mobile, test frame has been fully assembled and attachment of RPF components will occur over the next month. Development of the control system for test platform has begun. A fully functional system will be complete and ready for validation by the start of the local growing season.

Appendix G

Doppler Raman spectroscopy development

Doppler Raman (DR) spectroscopy makes use of short laser pulses to impulsively excite molecules with vibrational frequencies with an oscillation period that is shorter than the pulse duration – the shorter the pulse, the greater the highest Raman frequency that can be excited (see Fig. 1). The fiber laser that we are using for this project produces ~ 130 fs pulses, which are relatively long and therefore only allow for the excitation of a restricted band of vibrational frequencies. In order to excite a wider band of frequencies, we must compress the pulse approximately 8x, to a short enough duration – about 20 fs. In Q1, we focused on the design and modeling of the pulse generation system. Our simulation predicts pulses short enough to excite vibrational modes > 1600 cm^{-1}. A Fourier transform of the pulse intensity profile provides a measure of the relative amplitude of DR detection efficiency. The DR excitation efficiency is given in Fig. 1a for the Y-Fi laser pulse and for the spectrally broadened and compressed pulse. Clearly, the broadened pulse will be able to excite many more Raman frequencies than the Y-Fi pulse itself. Nevertheless, we see in both cases that DR is an excellent detector of low-frequency vibrational modes and presents a unique opportunity to probe the use of low frequency Raman vibrational spectroscopy for chemical identification. This is difficult to do with standard Raman measurement techniques. As of the end of Q2, we have ordered the vast majority of parts needed for the first prototype, enabling us to start construction in the lab. The primary system component that we ordered was the Yb:fiber laser from KM Labs. This laser arrived in November and we have tested it thoroughly. When the system was delivered, we worked with the technician to optimize the pulse performance. During Q2 we also began work on the pump/probe interferometer. While continuing the design of the short pulse system component, we moved ahead on the interferometer component by simply launching our long 130 fs pulse into the interferometer.

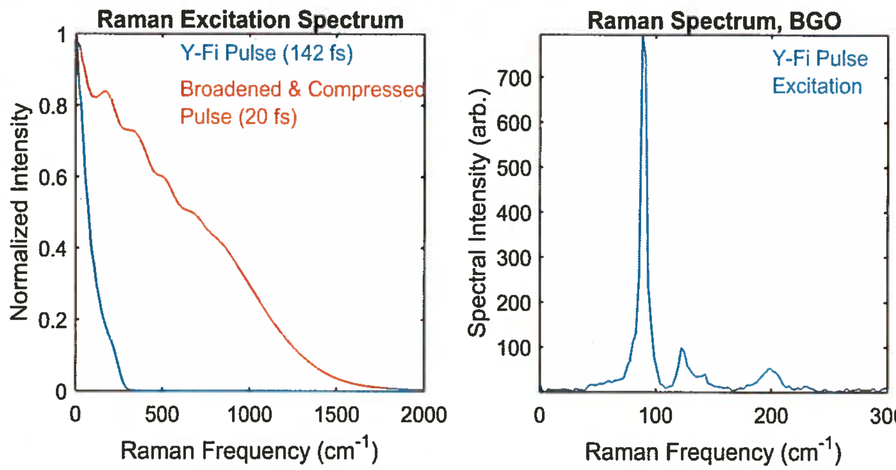

Fig. 1 (a) Expected Raman excitation spectrum for both the Y-Fi laser pulse and for the spectrally broadened and compressed pulse. **(b)** Measured Raman spectrum from a BGO crystal, demonstrating the excitation of vibrational frequencies within the bandwidth of the Y-Fi pulse.

Ground-truthing field measurements of roots

We tested root pulling, cleaning and imaging of field plants from the last field season for ground truthing. Sixty pulled root crown samples (30 accessions with 2 replicates each) were scanned and analyzed for 3D root architecture traits using X-Ray computed tomography, as well as imaged and analyzed for 2D root architecture traits using the DIRT software package (Bucksch et al. 2014). After data standardization and the removal of 3 sample outliers, fourteen 3D traits and eighteen 2D traits exhibiting normal (Gaussian) distributions were retained for analysis, while future work will attempt to incorporate additional useful traits. Based on Pearson correlation tests (Bonferroni-adjusted p-value < 0.05), Root Pulling Force (RPF) was significantly correlated with eight 3D root traits (surface area, volume, total root length, convex hull volume, number of root tips, maximum network width, median number of roots, maximum number of roots) and two 2D root traits (area, median width). Pearson's r coefficients between RPF and these significant traits ranged from 0.47 to 0.75, indicating a strong association between RPF and root architecture.

Build value model

This project is recruiting multiple technologies to attain an ambitious goal of identifying root phenotypes and their associated genetic loci. As such, the breeding values of that resulting information is what anchors the value model that we develop. Overall, we are pursuing the value modelling exercises in this project at two levels. First, the techno-economic model we are developing is an ongoing exercise that engages each of the co-PIs in consideration of utility/cost tradeoffs as they develop and adapt their technological contributions to the high throughput phenotyping data outputs of this project and the use those to identify genetics governing root traits in maize. How do we optimize the breeding value of this project and the probability of results being carried forward by other partners, particularly commercial partners, after current funding has ended? The techno-economic model considers the costs and value of each technology within the context of the goals of this project. It is acknowledged that each of the technologies has broader areas of commercial application such as in precision agriculture, soil testing, or geospatial data management. However, for the purposes of this project we are limiting the scope of our techno-economic model to the costs and value contributions of each component technology to the objectives of this ROOTS project. We confront two main conceptual challenges in adapting the engineering methodologies of techno-economic analysis to the breeding industry. One of them is the fundamental scientific nature of genomic information being pursued. Such scientific and technical information is discovered at some cost, but once discovered is, in theory, freely available for multiple breeding programs to utilize. This undermines typical notions of marginal costs that are embedded in most techno-economic models, but may be replaced by assumptions of average cost accounting, together with assumptions regarding risks, uncertainties, timeframes, and marginal benefits of each component's contribution to the value of these results.

The second level of this project seeks to address the second major conceptual challenge: that the ultimate commercial value of the genomic information being pursued under this project, such as in terms of breeding values of identified lines, is not well characterized. The private valuation by maize breeders for such genomic or breeding value information is driven by their expectation that farmers will have a higher willingness to pay for maize varieties that contain enhanced root traits. This private valuation by farmer, however, is almost certainly only a fraction of the larger societal and environmental values that would be realized by broad adoption of these traits (e.g. drought assurance or C sequestration services). Thus, a fundamental commercial question to be answered is farmers' private willingness to pay for enhanced root traits, and thus commercial adoption potential of maize varieties bred with them. Over years 1 and 2 (Q1-Q8) we are engaging in agricultural economic research to establish the value of these traits in US and world maize agriculture (following Useche 2009 and Wossink & Swinton 2007).

Benefits that the project has brought to Colorado:

This project is directly supporting multiple graduate and undergraduate students. Techno-economic development benefits are also being explicitly evalulated (see value modeling description above). Finally, this work will increase the capabilities of CSU's agricultural research center as a drought research facility. The US currently lacks a national research site for agriculture that provides consistent drought environments. The Colorado State University field site in Fort Collins (ARDEC) is a particularly good location for drought experiments, being located in a semi-arid climate allowing consistent applications of drought regimes, while still being in a commercial maize-growing region. We hope to leverage this favorable environment and research infrastructure towards a national research site for understanding how maize alleles respond to drought.

References:

Bucksch A, Burridge J, York LM, Das A, Nord E, Weitz JS, Lynch JP (2014) Plant Physiol 166: 470-486

Useche, Pilar, Bradford L. Barham, and Jeremy D. Foltz. "Integrating Technology Traits and Producer Heterogeneity: A Mixed-Multinomial Model of Genetically Modified Corn Adoption." American Journal of Agricultural Economics 91, no. 2 (2009): 444-61.

Wossink, Ada, and Scott M. Swinton. "Jointness in Production and Farmers' Willingness to Supply Non-Marketed Ecosystem Services." Ecological Economics 64, no. 2 (2007/12/15/ 2007): 297-304.