All Day Carbon Capture and Sequestration through Molecular and Phase-Change Hybrid Module

Abstract: As the world slowly transitions from conventional fossil fuels to renewable forms of energy, environmentally friendly CO\textsubscript{2} capture is urgently needed. Currently, liquid amine and ionic liquid-based systems are utilized for this purpose which both require large industrial point source for efficient performance. Liquid amine scrubbing leads to the formation of stable carbamate salts with high enthalpy of formation, and it is therefore difficult to recover the initial liquid for cyclic operation while ionic liquid-based systems suffer from high operational cost. Solid-state chemisorbent materials provide a viable solution for direct air capture of CO\textsubscript{2} (DAC) with stable and long-cyclic performance. However, they require high temperature for the CO\textsubscript{2} desorption. Here, we propose a new transformative paradigm to conduct all-day DAC with a hybrid solar-driven module. On the energy aspect, the module harvest and store full spectrum of solar energy and generate temperature of >100 °C in 24/7 manner for continuous operation of the system. On the process aspect, the module harvests CO\textsubscript{2} and humidity from air and provides valuable products of CaCO\textsubscript{3} and drinking water. We envision this stand-alone paradigm open a new path to address global emissions and consequent environmental challenges.

Introduction. Global CO\textsubscript{2} emissions have increased at an alarming rate of approximately 40% in the last 10 years,\textsuperscript{1} with the rate expected to double by 2050.\textsuperscript{2} Consequently, the reduction of environmental CO\textsubscript{2} has major implications on the global society\textsuperscript{3}, and its capture is being viewed as one of the most prominent means of decarbonization. Demands for efficient CO\textsubscript{2} capture technologies are driving the exploration of different mechanisms.\textsuperscript{4} Current commercial technologies employed for CO\textsubscript{2} capture include the use of amine-based solvents, mainly monoethanolamine (MEA), diethanolamine, and methyldiethanolamine.\textsuperscript{5–7} However, these forms of capture lead to the formation of stable carbamate/carbonate salts\textsuperscript{8}, making it difficult to recover the amine-based solvent for cyclic operation. Furthermore, the large enthalpy of CO\textsubscript{2} capture reaction corresponds to highly energy intensive and costly cyclic systems.\textsuperscript{9,10} Amine-based systems suffer from low CO\textsubscript{2} capture capacity,\textsuperscript{10} toxicity,\textsuperscript{11} loss of reagent due to evaporation, and equipment corrosion.\textsuperscript{12} While over the half the CO\textsubscript{2} emissions are from large, industrial point sources, the remainder of this emission are from small mobile source which is dispersed in the air. Thus, an economical pathway to reduce atmospheric level of CO\textsubscript{2} is becoming a critical issue.
Direct air capture of CO$_2$ (DAC) is a promising approach to address this global challenge. The materials for DAC are divided in two categories of chemisorbent and physisorbent materials. While the desorption process in the latter category require less energy, these materials do not high CO$_2$ absorption capacity and absorption selectivity. They absorb a large portion of water from humid air along with CO$_2$ leading to their inefficient performance. On the other side, the chemisorbent material have high capacity and selectivity, but need a source of thermal energy with temperature of $\sim$100 °C for desired cyclic performance.

**Objectives.** Here, we aim to develop a disruptive paradigm for efficient and economical DAC process through a solar-driven hybrid module. This hybrid system operates stand-alone in 24/7 manner with no external energy input, harvests atmospheric CO$_2$ and produces drinking water and CaCO$_3$ as byproducts.

**Approach.** Recently, we combined the physics of molecular energy and latent heat storage to introduce an *integrated* harvesting and storage hybrid paradigm for 24/7 energy delivery with temperature of $>$ 100 °C. The hybrid paradigm utilizes heat localization during the day to provide a harvesting efficiency of 73% at small-scale and $\sim$90% at large-scale. Remarkably, at night, the stored energy by the hybrid system is recovered with an efficiency of 80% and higher temperature than that of
the day, in contrast to all the state-of-the-art systems. This new concept is recently disclosed by PI and Co-PI in Joule (Cover article)\textsuperscript{13}. This concept provides required energy for CO\textsubscript{2} desorption of chemisorbent materials. In this program, we choose aqueous solution of Ca(OH)\textsubscript{2} as the heat transfer fluid (HTF). This fluid is an effective medium to absorb CO\textsubscript{2} and convert it to drinking water and CaCO\textsubscript{3}. This concept is demonstrated in another collaborative work by PI and Co-PI\textsuperscript{14}. We will initially synthesize amine-decorated mesoporous silica (ADMS) particles with high CO\textsubscript{2} absorption capacity. These ADMS particles have high active surface area for CO\textsubscript{2} capture and high selectivity of CO\textsubscript{2} adsorption compared to H\textsubscript{2}O (i.e. > 94% CO\textsubscript{2} even in high humid air) making them a suitable choice for humid hot environments\textsuperscript{15}. Once developed, we will characterize chemical composition, microstructure and CO\textsubscript{2} absorption of ADMS particles to optimize their performance and rationally design dimensions of each component in the hybrid module. The ADMS will be included underneath of the PCM material as shown in Fig. 1 to avoid any interruption in the solar irradiation path through the hybrid module. The ADMS is in direct contact with air to absorb CO\textsubscript{2}. Once saturated with CO\textsubscript{2}, the air flow to the ADMS compartment will be stopped and the hot fluid will be circulated over the ADMS particles to absorb the CO\textsubscript{2} and re-activate the ADMS particles. The flow rate of HTF is adjusted to maximize CO\textsubscript{2} dissolutions with minimal heat losses. The hot solution of Ca(OH)\textsubscript{2} will lose some of it thermal energy in the desorption process and the outlet HTF from the ADMS compartment has lower temperate than the inlet stream. The outlet Ca(OH)\textsubscript{2} solution saturated with CO\textsubscript{2} is taken to a reservoir where the solution converts to drinking water and CaCO\textsubscript{3} as demonstrated by PI\textsuperscript{s}\textsuperscript{14}. The drinking water may be re-combined in the initial Ca(OH)\textsubscript{2} solution to re-circulate through the cycle or could be used as a byproduct of the system. We should add that this approach of carbon capture has value proposition as the byproduct CaCO\textsubscript{3} is more valuable than the initial solution of Ca(OH)\textsubscript{2}. Note
that during the day, the thermal energy for ADMS desorption will be provided by PCM, but at night the majority of thermal energy is provided by MSM. That is, the system runs continuously 24/7 to capture CO\textsubscript{2} and convert it to byproducts. Furthermore, the system has the potential to be implemented in point-source CO\textsubscript{2} emission settings with similar performance.

**Outcomes and Time Frame.** This project provides a transformative paradigm to capture atmospheric CO\textsubscript{2} and to convert it to valuable byproducts of water and CaCO\textsubscript{3}. The project will start in August 2020 once funded and will run for 18 months. **Milestone 1 (6 mo):** Synthesis of high capacity ADMS, **Milestone 2 (12 mo):** Demonstration of efficient CO\textsubscript{2} capture and sequestration, **Milestone 3 (18 mo):** Demonstration of 24/7 performance of the system with no power input

**Progress and Management Reporting.** The PI and Co-PI are committed to provide required progress report and presentations based on the guidelines of the program.

**Equipment and Facilities.** The NanoTherm lab is equipped with a solar simulator with an optical concentrator up to 50x concentration and all metrology resources to examine performance of the hybrid module. Dr. Lee’s group is equipped with 15 fume hoods in the SERC building for experiments ranging from organic and inorganic synthesis to surface science.

**Internal and External Funding.** We received funding from Petroleum Research Fund to study nano-scale physics of CO\textsubscript{2} hydrate structures, $110 k. We received Advanced Manufacturing Fund to develop large-scale module for solar energy harvesting and storage, $50 k.

**Future Proposal Submissions.** We submitted a proposal to the DOE solicitation (DE-FOA-0002243) on the solar energy harvesting and storage on 6/15/2020. We are working on a proposal of atmospheric harvesting of CO\textsubscript{2} to DOE solicitation (DE-FOA-0001953) which is due 7/22/2020.
BIOGRAPHICAL SKETCH (Hadi Ghasemi, PhD)

(a) Professional Preparation

Univ. of Science and Tech. Iran Materials Science Bachelor of Science, 2003
Sharif University of Technology Iran Materials Science Master of Science, 2007
University of Toronto Canada Mech. Engineering PhD, 2011

(b) Appointments

Sept. 2019 - Present Cullen Associate Prof. of Mechanical Eng., University of Houston
Sept. 2014 - 2019 Bill D. Cook Assistant Prof. of Mechanical Eng., University of Houston
Dec. 2011- 2014 Postdoctoral Associate, Department of Mechanical Engineering, MIT

(c) Publications

Most Closely Related to the Proposed Project


Other Significant Products


2) Yanfei Xu, Daniel Kraemer, Bai Song, Zhang Jiang, Jiawei Zhou, James Loomis, Jianjian Wang, Mingda Li, Hadi Ghasemi, Xiaopeng Huang, Xiaobo Li, Gang Chen, “Nanostructured Polymer Films with Metal-like Thermal Conductivity”, Nature Communications, 10, 1771, (2019).
https://pubs.rsc.org/en/content/articlelanding/2019/mh/c8mh01291a#!divAbstract

http://www.nature.com/articles/ncomms13395

http://www.nature.com/ncomms/2014/140521/ncomms4942/full/ncomms4942.html

(d) Synergistic Activities


2. Co-Chair of ASME NEES (Nanoengineering for Energy and Sustainability) committee. Organized micro/nano poster forum (Topic organizer) in IMECE conferences (2015 and 2016). The forum allows graduate students and post-doctoral associates to network with leaders and advocates in micro- and nanotechnology and to be recognized for their hard and creative work; Track chair of “micro and nano technology in energy systems” in ASME 2014, 8th International Conference on Energy Sustainability; Topic organizer of “Solar thermochemistry and solar fuels” and ”micro and nano technology in energy systems” in IMECE 2014.

3. Established a quarterly platform for K-12 students to visit PI’s research group. The PI teaches the students about research in micro/nano engineering. The involved students in these tours conduct hands-on experiments. (Oct. 2014-now); Created summer internship opportunity for undergraduate students through SURF, PURS, and Honor programs at the University of Houston.

PROFESSIONAL PREPARATION

Rice University
Houston, TX
Chemistry
B.A. 1985

Harvard University
Cambridge, MA
Chemistry
Ph.D. 1991

California Institute of Technology
Pasadena, CA
Chemistry
Postdoc 1991–93

APPOINTMENTS

2012–present
Assoc. Dean Research, College of Natural Sciences & Mathematics, UH, Houston, TX

2006–present
Cullen Distinguished University Chair, Department of Chemistry, UH, Houston, TX

2004–2012
Associate Chair, Department of Chemistry, UH, Houston, TX

2003–present
Professor of Chemistry, Department of Chemistry, UH, Houston, TX

1999–2003
Associate Professor of Chemistry, Department of Chemistry, UH, Houston, TX

1993–1999
Assistant Professor of Chemistry, Department of Chemistry, UH, Houston, TX

CLOSELY RELATED PRODUCTS (five products most closely related to the proposed project)

"Full Spectrum Solar Thermal Energy Harvesting and Storage by a Molecular and Phase-Change Hybrid Material" V. Kashyap; S. Sakunkaewkasem; P. Jafari; M. Nazari; B. Eslami; S. Nazifi; Peyman Irajizad; M. D. Marquez; T. R. Lee; H. Ghasemi, Joule 2020, 3(12), 3100-311.


OTHER SIGNIFICANT PRODUCTS (out of 262 total peer-reviewed publications)


**SYNERGISTIC ACTIVITIES**

2013–present Co-coordinated the efforts of the UH College of Natural Sciences and Mathematics in conjunction with the UH College of Engineering to prepare a successfully-funded $4M proposal (with an additional $4M in state matching funds) to the Robert A. Welch Foundation to provide resources for establishing the Center of Polymer Excellence at the University of Houston ([http://www.uh.edu/nsm/chemistry/people/faculty/Harth/Polymer-Center.php](http://www.uh.edu/nsm/chemistry/people/faculty/Harth/Polymer-Center.php)). Subsequent efforts have centered on growth and outreach of the center, with an emphasis on building industrial collaborations.

2013–present Coordinated the efforts of the UH College of Natural Sciences and Mathematics in conjunction with the UH College of Engineering to write and submit a successfully-funded $1.5M proposal to the Howard Hughes Medical Institute to provide resources to establish the University of Houston STEM Center. The STEM Center is beginning its sixth year of service to advance local, state, and national teaching and learning for STEM students ([http://stem.uh.edu](http://stem.uh.edu)).


2012–present Associate Dean for Research for the College of Natural Sciences and Mathematics at the University of Houston.

2004–present Notable continuous committee service to the University of Houston community: University of Houston Undergraduate Health Professions Advisory Committee (2004–present), University of Houston Faculty Senate & Executive Committee of the Faculty Senate (2004–present), and Phi Beta Kappa, Mu of Texas Chapter, Organizing Committee and Advisory Committee (2013–present).
References


(4) Ritter, J. A.; Ebner, A. D. State-of-the-Art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries; 2009; Vol. 44. https://doi.org/10.1017/CBO9781107415324.004.


