Catalyst: The Roles of Chemistry in Clean Water for All

Young-Shin Jun*

Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis

*Email: ysjun@wustl.edu
Webite: http://encl.engineering.wustl.edu/

Bio

Dr. Young-Shin Jun is a Professor of Energy, Environmental and Chemical Engineering and the Director of the Environmental NanoChemistry Laboratory at Washington University in St. Louis. She solves important energy and environmental challenges using nanoscale interfacial reactions and nucleation. Her research interests in clean water are novel materials development, membrane processes, resource recovery, and managed aquifer recharge. She received a 2011 U.S. National Science Foundation CAREER award, and she was named a 2015 Kavli Fellow by the U.S. National Academy of Sciences, a 2016 Frontier of Engineering Fellow by the U.S. National Academy of Engineering, and a 2019 American Chemical Society Fellow.

eTOC blurb (80 words)

Understanding nanoscale interfacial reactions unlocks the chemistry controls that are critical for clean water generation. This Catalyst discusses three important roles of chemistry in clean water: Understanding and controlling evolving interfaces induced by nucleation, deciphering and utilizing hidden interfaces in nanoconfined spaces, and harnessing interfaces with functionalized surfaces. Chemically guided developments of new materials and technologies for purifying clean water can bring all water resources back to one H_2O, which supports life for all people.

Water seems to be everywhere and not a critical resource. However, in fact, our supply of clean water is limited, and life cannot exist without it. In 2016, the United Nations (UN) set up 17 sustainable development goals (SDGs),[1] and Goal 6 is to "ensure availability and sustainable management of water and sanitation for all." Based on the 2022 SDGs report, meeting drinking water, sanitation, and hygiene targets by 2030 requires a fourfold increase in the pace of progress. At the current rates, in 2030, 1.6 billion people will lack safe drinking water and 2.8 billion people will lack safe sanitation.[1]

Our water supply is inseparably linked to climate, and the recent acceleration of climate change has caused natural disasters, heat waves, and water shortages. Climate change has brought warmer weather and drought-driven water salination, and anthropogenic activities have created more nutrient-rich water and increased atmospheric CO_2 concentrations. Such confluences have caused harmful algal blooms (HABs) to occur more often, more intensely, and in more water systems. Considering the climate-induced changes in the natural water cycle and the engineered water use cycle, we need to design sustainable water management (SWM) systems that support current and future populations with minimal environmental impacts. In these SWM systems, nanoscale interfacial chemistry plays pivotal roles in producing and managing clean water.

Solid–water interfaces in environmental systems can change the fate and transport of pollutants, nutrients, and nanoparticles, affecting the efficiency of water treatment processes. Complex interactions on surfaces or in nanoconfinement can determine the behaviors of different ions and ion-pairs, radical formation, and nanoparticle nucleation near interfaces. Hence, nanoscale interfacial chemistry is a key to better understanding, predicting, and controlling reactions that can promise more clean water through sustainable practices. As Figure 1 illustrates, chemists have tremendous opportunities to elucidate the nanoscale picture of (1) how the interfaces evolve, (2) how nanoconfinement and hidden pore interfacial spaces control ion hydration, binding, and reaction kinetics and mechanisms, and (3) how chemically modified, highly reactive surfaces can promote and facilitate water purification.

Evolving interfaces: Nucleation

Environmental interfaces are not chemically inert and steady. Their chemical structures and consequent chemical and physical properties are continuously evolving to respond to the surrounding water chemistry. Moreover, the surface charge at a solid–water interface induces an electric double layer (EDL), influencing the distribution of ions, organics, and water molecules. The surface heterogeneity can also modulate the interfacial energy of newly formed nanoparticles, controlling nucleation rates and the aggregation of these newly formed nanoparticles. These interfaces with newly formed nanoparticles act as new reactive surfaces with different chemical moieties, atomic structures, and morphologies, determining the subsequent reaction mechanisms and kinetics.

Such solid nucleation exerts exceptional control on evolving interfaces during water treatment (Figure 1A-i).[2] As an example in desalination membrane processes, common foulants are $CaCO_3$, $CaSO_4$, silicate, and iron (hydr)oxides (Figure 1A-ii, iii, iv, and vi). Membrane scaling can form in solution (homogeneous nucleation) or on a membrane surface (heterogeneous nucleation). The impacts of these two mechanisms can differ. Heterogeneous nucleation occurs in early stage scaling, controlling the scale location and membrane permeability and decreasing the water flux. Heterogeneous nucleation has a lower energy barrier than homogeneous nucleation, resulting in faster nucleation.[2] To reduce fouling, many attempts have been made to modify membrane surfaces—endowing them with the desired hydrophilicity/hydrophobicity, surface morphologies, chemical functional groups, and surface charges—and to engineer membrane pore structures. Outstanding challenges for chemists to address include the synthetic chemistry of membranes, the evolution of membrane structures (*e.g.,* swelling of polymeric membranes), membrane surface interactions with aqueous precursor molecules, and the nucleation and crystallization of inorganic foulants.

As an example in nutrient-rich wastewater treatment, the formation of ammonia or phosphate-containing solids can capture nutrients, preventing the occurrence of HABs, and allow to reuse them as a slow-release fertilizer. One highly developed crystallization method forms struvite ($NH_4MgPO_4{\bullet}6H_2O$), hydroxyapatite ($Ca_5(PO_4)_3(OH)$), and iron phosphate. While micron-sized crystals are better for plant growth, they are harder to collect. On the other hand, millimeter-sized crystals, while easier to collect, might not provide sufficient phosphate for plant growth. One new method resolves these dilemmas by nucleating nanoscale calcium phosphate seeds and wollastonite ($CaSiO_3$) in hydrogels (Figure 1A-v).[3] Thus, the mineral-hydrogel composites can recover phosphate effectively, and the nutrient-recovered composites can be recycled to provide enough phosphate for non-traditional agricultural systems and biorefineries (Figure 1A-vii).[3,4] Many different types of nucleation-controlled water treatment and nutrient recovery and reuse systems also offer excellent research opportunities for chemists. Here, we need a better understanding of the mechanisms and kinetics of the nucleation, growth, and aggregation of nanoscale solid phases and the evolutions of their reactive surface areas, along with their phase transformation, in water systems. This improved understanding will enable us to tune particle sizes and shapes, surface facets, and mineral phases for more effective reuse, e.g., as fertilizer or chemical feedstock.

Hidden interfaces: Nanopores

Nanopores filled with water are ubiquitous, including shales and sandstone in energy-related subsurface operations, desalination membranes (Figure 1B-ii), periodic porous materials (*e.g.,* zeolite, Figure 1B-iv), and catalytic nanomaterials (Figure 1B-v). Because nanopores provide a high surface area, control molecular transport, and promote noticeably high chemical conversion, more novel nanoporous materials will be considered in engineered water treatments as catalysts, separation membranes, and sensing probes.[5] As previously mentioned, interfaces have higher chemical reactivity than the bulk phase. Nanopores are full of hidden and elusive interfaces. Often, experimental observations are challenged to describe nanoscale pores. Understanding the chemical and physical properties in nanopores and their reaction kinetics will unlock their great potential for water treatment. Nanopores cause water to behave differently from in the bulk, decreasing its dielectric constant, density, surface tension, and freezing temperature. These changes can further promote dehydration of hydrated ions, decrease the number of hydrogen bonds, and cause solvation frustration in nanopores.[6] However, it is still unclear how nanoconfinement affects solute-solute and solute-surface interactions, which can influence local ion and ion-pair concentrations, pH, pK_a, ion adsorption, and nucleation in nanopores.[6] Furthermore, the limited space and high curvature can cause the EDL in nanopores to be overlapped, and the surface atomic structure in nanopores can possess more defects and be less crystalline than without nanoconfinement. Hence, *in situ* probing these unique nano-environments and hidden interfaces is vital to developing nanoconfinement-enabled water treatments.

The master variable of water chemistry is pH. Nanopores make describing this simple yet most important parameter extremely difficult. Recently, using surface enhanced Raman spectroscopy and plasmonic nanoprobes (Figure 1B-i and iii), Zhu et al. (2022) found that in negatively charged 3 nm silica nanopores, anion concentrations were enhanced, whereas cation concentrations were suppressed, causing electroneutrality breakdown. To alleviate the breakdown, proton transport can be facilitated, lowering the pH in the nanopores by as much as two units compared to the bulk pH. The next open question for chemists is how ion concentrations in nanopore solutions are related to those in the bulk solution at equilibrium. Describing the distribution of toxic ions between nanopore solutions and the bulk solution can help understand the fate and transport of toxins in water treatment.

By utilizing the abnormal reactivity and unexpected reaction pathways in nanopores, Yang et al. (2019) demonstrated that 2 nm Fe_2O_3 nanoparticles inside a 7 nm diameter carbon nanotube (Fe_2O_3@FCNT-H, Figure 1B-v) generated singlet oxygen ($^1O_2$) as the main reactive intermediate and promoted organic compound degradation kinetics, whereas without confinement, Fe_2O_3 nanoparticles showed traditional Fenton-like reaction pathways with H_2O_2, generating hydroxyl radicals (•HO).[7] However, the detailed mechanisms of these nanoconfinement-facilitated reaction kinetics need further examination. Of even greater interest, elucidating the mechanisms of nanoconfinement-facilitated catalytic reactions can be a promising research direction for chemists.

Harnessing interfaces

To achieve more efficacious water treatment, we can further modify reactive surfaces with desired chemical functional groups, surface roughness, hydrophilicity/hydrophobicity, and functional single atom catalysts and nanoparticles. With such modifications, we can elevate contaminant degradation rates, increase reactive radical species generation rates in advanced oxidation processes, and reject specifically sized, charged, or dielectric ions through membranes. The methods to harness interfaces for clean water can be realized through myriad pathways.

One of the most recent classes of modified interface applications for water purification is photothermal interfaces for water evaporation (*i.e.,* solar stream generation) and photothermal membrane distillation. The photothermal effect describes a direct conversion where the photoexcitation of materials produces thermal energy (heat).[8,9] Photothermal materials with high efficiencies of light-to-heat conversion include inorganic materials (noble metals and semiconductors) and organic materials (carbon-based nanomaterials and conjugated polymers). Among them, polydopamine (PDA, Figure 1C-i) is a biodegradable, environmentally benign photothermal material. Furthermore, the size of PDA particles can be tuned to for maximum absorption of light in a spectrum similar to that of sunlight (Figure 1C-ii), and they can be mechanically interlocked by bacterial nanocellulose (Figure 1C-iii and iv). These thermally-engineered photothermal membrane distillation units allow using room temperature feedwater to generate vapor pressure across the membrane to generate clean water. The surface temperature of membrane reaches around 80°C, facilitating water vapor generation and exhibiting bactericidal effects (Figure 1C-v).[8] Photothermal interfacial applications for water treatment enable water purification in developing countries and rural communities. Furthermore, photothermal water treatment technologies provide inexpensive, modular, decentralized, and accessible ways to clean water, reducing energy consumption and the cost of clean water production. Modular, decentralized water treatment can be particularly effective during the more frequent natural disasters caused by climate change and unexpected future pandemics. While these new photothermal membranes are promising for providing clean water, challenges remain in translating such a novel invention from the laboratory scale to devices or utility-scale plants. To realize the practical applications of chemistry-driven invention, we will need to improve the scalability, chemical and mechanical stability, and sustainability of photothermal membranes.

Challenges and Opportunities

To probe such evolving interfaces triggered by the surrounding complex water chemistry, first, *in situ* real-time characterization techniques of solid nucleation at interfaces are crucial. Second, with these new characterization tools, we must obtain the quantitative descriptors of nucleation processes in diverse water systems. Third, characterizing interfacial structures is essential to accurately predict adsorption and nucleation. The interfacial solution structures and hydration properties of ions at interfaces can define the chemical speciation, nucleation driving force, and the attractive and repulsive forces for precursor molecules and newly formed nanoparticles.[6] Fourth, we need to account for complexity in water systems. For example, the first complexity is that 97% of the water on Earth is saline, and water gets saltier with drought. Flowback water from unconventional energy recovery sites and effluents from desalination plants can be saltier than seawater. For such high salinity water, conventional activity coefficient models are insufficient, and activity models like the Pitzer or specific ion interaction theory (SIT) are used to represent the thermodynamics of the system, but they still cannot fully describe the ion activity for such high saline environments. A second complexity is the presence of organics and microorganisms and diverse types of interfaces (e.g., rigid single- or multi-phase solid surfaces, soft polymeric substrates, cell membranes, and liquid–liquid interfaces). A third complexity is related to the surface charge at a solid–water interface. Because EDL can alter reactions kinetically and thermodynamically, the structure of the EDL is fundamental to examine ion adsorption and nucleation. However, inhomogeneous structures in the EDL (overcharging phenomenon) can result from ion–ion correlations. These inhomogeneous charge distributions can further influence the water orientation and the pH at the interface, modifying ion adsorption and heterogeneous nucleation.[2]

Key nanoscale interfacial chemistry research directions offer exciting opportunities for chemists to contribute to clean water generation. Chemists can provide understanding and control of the evolving interfaces induced by new solid phase nucleation; chemists can decipher and actively utilize hidden interfaces in nanoconfined spaces; and chemists can harness interfaces with functionalized surfaces. Elucidating nucleation mechanisms and crystallization pathways can further provide new opportunities in resource recovery from highly saline water sources and valorize them as a chemical feedstock, which will enhance a circular economy closely connected with water resource management.[10] It can also present clues for water quality changes caused by managed aquifer recharge and lead-containing pipelines. Chemical insights into nanoscale dynamic interfaces for clean water can also be applied to other interface-enabled chemical processes in batteries, photocatalysis, direct CO_2 capture, and durable CO_2 storage. Machine learning and artificial intelligence tools can also be useful for predicting collective performance by multivariable water and material conditions.

After all, there is only one water. Chemically guided developments in new materials and technologies for purifying clean water can bring all types of water resources back to one H_2O, supporting life for all people.

Acknowledgements

The author acknowledges support from the United States National Science Foundation Environmental Engineering Program (CBET-1604542) and Environmental Chemical Science Program (CHE-1905077) and the United States Environmental Protection Agency (Assistance Agreement No. 840084). The article has not been formally reviewed by the EPA. The views expressed in this article are solely those of the author and do not necessarily reflect those of the Agency. The EPA does not endorse any products or commercial services mentioned in this publication.

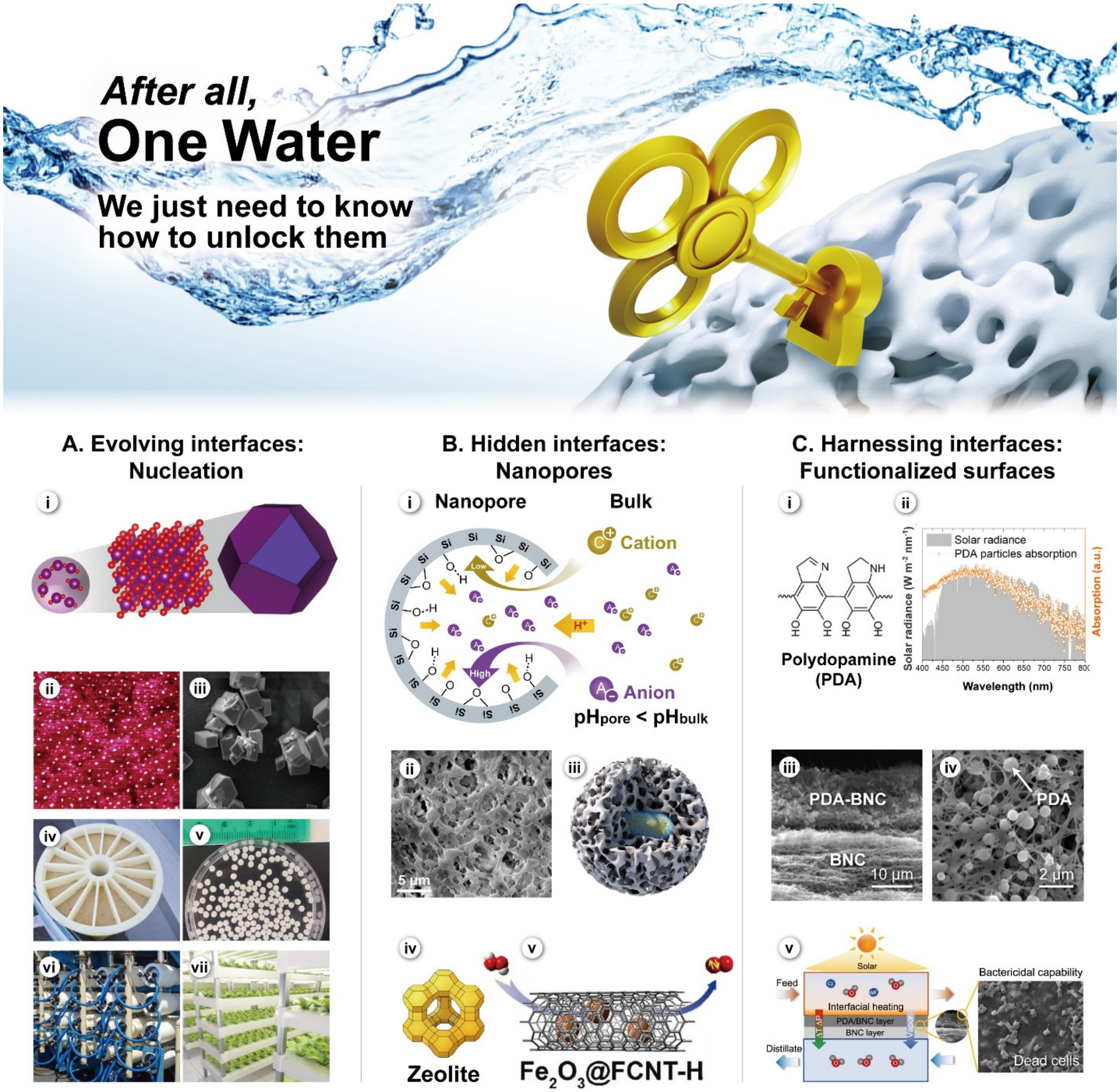

Figure 1. Bringing all water resources back to one clean water through chemistry. (A) Evolving interfaces: Nucleation. (B) Hidden interfaces: Nanopores. (C) Harnessing interfaces: Functionalized surfaces. (A-i) Nucleation pathways from prenucleation clusters, to critical nuclei, to thermodynamically stable faceted crystals).[2] (A-ii) Atomic force microscopy image of calcium carbonate nucleation on a (100) surface of quartz. Reproduced from Li et al. (2018) with permission.[11] Copyright 2018 Springer Nature. (A-iii) Calcite formation on a membrane surface. (A-iv) End view of a spiral wound reverse osmosis (RO) membrane unit in an RO train (A-vi) in the Carlsbad desalination plant, California, USA. RO membranes commonly suffer from

inorganic scale fouling by calcium carbonate, calcium sulfate, silicate, and iron oxides. (A-v) Calcium phosphate-wollastonite ($CaSiO_3$) seeded alginate hydrogel composites for phosphorus recovery/removal from phosphorus-rich water effluent.[3] (A-vii) The recovery and recycling of nutrients based on mineral-hydrogel composites can improve the circular economy of non-traditional hydroponic agriculture.[4] (B-i) The pH in silica nanopores at high salinity is lower than the bulk pH due to anions' propensity toward the nanopores, caused by the interface-induced polarization in nanopores. Reproduced from Zhu et al. (2022) with permission.[5] Copyright 2022 Elsevier. (B-ii) PVDF (polyvinylidene fluoride) membrane pores. Reproduced from Wu et al. (2018) with permission.[9] Copyright 2018 Royal Society of Chemistry. (B-iii) Illustration of a gold plasmonic nanosensor for detecting aqueous chemistry in nanopores.[5] (B-iv) Nanopores in zeolite, which is commonly used in environmental applications. (B-v) 2 nm Fe_2O_3 nanoparticles inside the 7 nm diameter of a carbon nanotube (CNT) in nanoconfinement (Fe_2O_3@FCNT-H). Unexpectedly, Fe_2O_3 nanoparticles in nanoconfinement can generate $^1O_2$ as the main reactive intermediate and promote organic compound degradation. Reproduced from Yang et al. (2019) with permission.[7] Copyright 2019 National Academy of Sciences. (C-i) Structure of polydopamine (PDA) that was used to modify the membrane surface for higher photothermal efficiency. (C-ii) The size of polydopamine particles can be tuned for maximum absorption of light. (C-iii) Side view of a bilayer photothermal membrane for thermal engineering. The membrane consists of a bacterial nanocellulose layer (BNC) supporting layer and a PDA mechanically interlocked BNC top layer. (C-iv) Top view of the photothermal membrane. (C-v) Photothermal membrane distillation setup. Images (C-ii, iii, iv, and v) were reproduced from Wu et al. (2021) with permission[8] Copyright 2021 Elsevier.

References

1. United Nations (2023). Goal 6: Ensure availability and sustainable management of water and sanitation for all. https://sdgs.un.org/goals/goal6.
2. Jun, Y.-S., Zhu, Y., Wang, Y., Ghim, D., Wu, X., Kim, D., and Jung, H. (2022). Classical and Nonclassical Nucleation and Growth Mechanisms for Nanoparticle Formation. Annual Review of Physical Chemistry *73*, 453-477. https://doi.org/10.1146/annurev-physchem-082720-100947.
3. Xiao, Z., Tan, A.X., Xu, V., Jun, Y.-S., and Tang, Y.J. (2022). Mineral-hydrogel composites for mitigating harmful algal bloom and supplying phosphorous for photo-biorefineries. Science of The Total Environment *847*, 157533. https://doi.org/10.1016/j.scitotenv.2022.157533.
4. Tan, A.X., and Jun, Y.S. (2023). Opportunities for Emerging Wastewater Phosphorus Recovery Technologies to Enable Circular Phosphorus Usage in Nontraditional Hydroponic Agriculture. ACS Agricultural Science & Technology. https://doi.org/10.1021/acsagscitech.3c00060.
5. Zhu, Y., Derami, H.G., Gupta, P., Gupta, R., Singamaneni, S., and Jun, Y.-S. (2022). Ionic surface propensity controls pH in nanopores. Chem *8*, 1-15. https://doi.org/10.1016/j.chempr.2022.07.021.
6. Bañuelos, J.L., Borguet, E.U., Brown, G.E., Cygan, R.T., DeYoreo, J.J., Dove, P.M., Gaigeot, M.-P., Geiger, F.M., Gibbs, J.M., Grassian, V.H., et al. (2023). Oxide- and Silicate-Water Interfaces and Their Roles in Technology and the Environment. Chemical Reviews. https://doi.org/10.1021/acs.chemrev.2c00130.
7. Yang, Z., Qian, J., Yu, A., and Pan, B. (2019). Singlet oxygen mediated iron-based Fenton-like catalysis under nanoconfinement. Proceedings of the National Academy of Sciences *116*, 6659-6664. https://doi.org/10.1073/pnas.1819382116.
8. Wu, X., Cao, S., Ghim, D., Jiang, Q., Singamaneni, S., and Jun, Y.-S. (2021). A thermally engineered polydopamine and bacterial nanocellulose bilayer membrane for photothermal membrane distillation with bactericidal capability. Nano Energy *79*, 105353. https://doi.org/10.1016/j.nanoen.2020.105353.
9. Wu, X., Jiang, Q., Ghim, D., Singamaneni, S., and Jun, Y.-S. (2018). Localized heating with a photothermal polydopamine coating facilitates a novel membrane distillation process. Journal of Materials Chemistry A *6*, 18799-18807. https://doi.org/10.1039/C8TA05738A.
10. Sedlak, D., Mauter, M., Macknick, J., Stokes-Draut, J., Fiske, P., Agarwal, D., Borch, T., Breckenridge, R., Cath, T., Chellam, S., et al. (2021). National Alliance for Water Innovation (NAWI) Master Roadmap. DOE/GO-102021-5617. https://www.nrel.gov/docs/fy21osti/80705.pdf.
11. Li, Q., and Jun, Y.S. (2018). The apparent activation energy and pre-exponential kinetic factor for heterogeneous calcium carbonate nucleation on quartz. Communications Chemistry *1*, 1-9. https://doi.org/10.1038/s42004-018-0056-5.