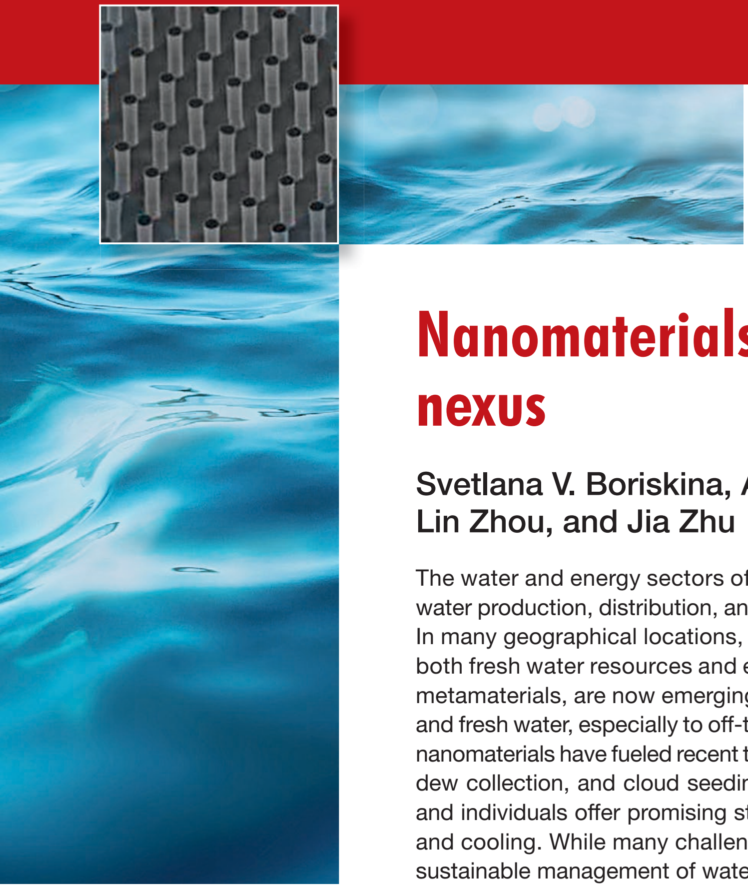

Nanomaterials for the water-energy nexus

Svetlana V. Boriskina, Aikifa Raza, TieJun Zhang, Peng Wang, Lin Zhou, and Jia Zhu

The water and energy sectors of an economy are inextricably linked. Energy is required in water production, distribution, and recycling, while water is often used for energy generation. In many geographical locations, the energy-water nexus is exacerbated by the shortage of both fresh water resources and energy generation infrastructure. New materials, including metamaterials, are now emerging to address the challenges of providing renewable energy and fresh water, especially to off-the-grid communities struggling with water shortages. Novel nanomaterials have fueled recent technology breakthroughs in solar water desalination, fog and dew collection, and cloud seeding. Materials for passive thermal management of buildings and individuals offer promising strategies to reduce the use of energy and water for heating and cooling. While many challenges remain, emerging materials and technologies improve sustainable management of water and energy resources.

Introduction

Many communities worldwide suffer from a shortage of fresh water resources (**Figure 1**a).[1] In some cases, the water shortage is caused by geography and climate, while in others, economic reasons prevail, including the high cost of industrial installation for energy production and water purification, and the absence of available credit resources to invest in new infrastructure.[2,3] One of the most promising strategies to address the challenges of providing renewable energy and fresh water, especially to off-the-grid communities, is to make use of the freely available sunlight as the renewable energy source as well as the vast cold universe as the heatsink. Fortunately, most of the regions with high water shortages have a natural advantage of abundant solar-energy resources (Figure 1b).[4]

Sunlight can be harnessed to fuel chemical reactions, generate electricity in solar cells, disinfect water, and produce heat for terrestrial thermal engines, water desalination plants, and residential use.[5–8] In turn, passive cooling of roofs, solar cells, and individuals via engineering solar absorptance and thermal radiation properties of materials can save energy through reduced use of air conditioning and other electricity-consuming active-cooling technologies.[9–15] Passive cooling of surfaces can also increase the efficiency of dew collection, helping to extract fresh water from the atmosphere.[16–19] Examples of nanomaterials developed to advance emerging technologies in the energy-water nexus are shown in **Figure 2**.[20–28] We discuss some of them in detail next, while also referring the reader to the available extensive review literature.[5,7,29–33]

Solar harvesting and cooling

To harvest solar light and heat, materials need to be spectrally engineered in the broad range of wavelengths (**Figure 3**a), covering both the solar spectrum (~0.3–2.5 μm wavelength) and the infrared emission spectrum of terrestrial emitters (~2–15 μm, depending on the emitter temperature).[7,34–38] An ideal absorber should possess high spectral absorptance in the solar spectrum range, low infrared emittance to reduce radiative heat losses, excellent durability at elevated temperature in air and water, and low cost, combining inexpensive starting materials and scalable coating processes.[39] Nonselective blackbody absorbers, including black fabrics, paints, and carbon-based materials, can be relatively inexpensive and provide high light absorption in a broad wavelength range.[40–42] However, they also emit thermal radiation over a broad range, which typically limits their use to either low-temperature applications such as conventional solar stills,[40,43,44] or applications relying on concentrating sunlight to small areas with lenses and reflectors.[6,34]

Svetlana V. Boriskina, Department of Mechanical Engineering, Massachusetts Institute of Technology, USA; sborisk@mit.edu
Aikifa Raza, Department of Mechanical and Materials Engineering, Masdar Institute, Khalifa University of Science and Technology, United Arab Emirates; aikifa.raza@ku.ac.ae
TieJun Zhang, Department of Mechanical and Materials Engineering, Masdar Institute, Khalifa University of Science and Technology, United Arab Emirates; tiejun.zhang@ku.ac.ae
Peng Wang, King Abdullah University of Science and Technology, Saudi Arabia; peng.wang@kaust.edu.sa
Lin Zhou, College of Engineering and Applied Sciences, Nanjing University, China; linzhou@nju.edu.cn
Jia Zhu, College of Engineering and Applied Sciences, Nanjing University, China; jiazhu@nju.edu.cn
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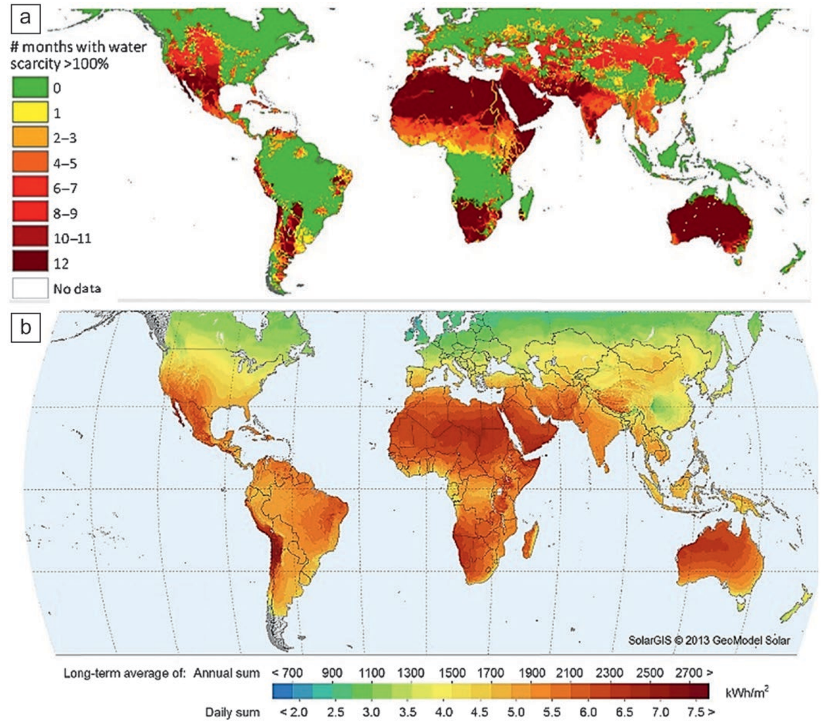

Figure 1. (a) Global water scarcity map. Many communities worldwide experience year-round water shortages. Adapted with permission from Reference 1. © 2016 AAAS. (b) Global solar irradiation map. Regions with water shortages typically have higher-than-average solar resources.[4]

Solar absorbers can be engineered by introducing metal nanostructures, such as nanoparticles, nanopores, and nanodisks, either on the absorber surface or inside its volume.[8,35,38,39,45–48] Surface plasmon modes excited by incident sunlight on these nanostructures facilitate efficient absorption of solar photons and conversion of their energy into heat. The nanostructured solar absorbers can be tailored to simultaneously offer high reflectance (i.e., low emittance) at longer wavelengths, thus facilitating heat trapping.[6,7,34,49–51]

Other approaches to enhance solar absorptance rely on the use of thin-film, photonic-crystal, and graded-index coatings as well as mesoscale structures combining photonic crystals and thin films with nanoparticles.[37,45,52–56] Lithography-free fabrication techniques yielding nanocomposite films and coatings are especially attractive for solar-thermal applications owing to their cost effectiveness and scalability.[39] An example of such scalable ultrathin nanocomposite film composed of silver (Ag) and glass (SiO_2) materials is shown in Figure 3b.[57] This nanocomposite absorber traps sunlight in a broad frequency range via excitation of multiple plasmonic resonances. These resonances are excited at several frequencies overlapping with the solar spectrum, and exhibit different spatial distributions of electromagnetic field, as shown in Figure 3b. Multifrequency response of this absorber stems from its complex mesosale internal structure. As surface plasmon resonances decay, their energy is dissipated as heat, elevating the absorber temperature. Furthermore, both sunlight and heat can be trapped inside internally hot, externally cool solar absorbers capped with optically transparent yet thermally insulating materials (Figure 3c). Highly porous aerogels and foams are excellent candidates for thermally insulating absorber coatings due to their extra-low thermal conductivity values. They can be made optically transparent for the solar light by reducing the size of the pores to the nanoscale,[43,58,59] and can increase efficiency of blackbody absorbers such as carbon black particles. The infrared camera image shown in Figure 3c illustrates the use of optically transparent silica aerogel insulation to trap heat inside a solar-thermal receiver illuminated by artificial sunlight from a solar simulator.[60,61]

Spectrally selective coatings are also finding use in daytime radiative cooling applications.[62–64] Thermal spectra of terrestrial emitters peak in the mid-infrared range (~7–15 μm). The earth's atmosphere is transparent within this range, known as the "atmospheric transparency window" (Figure 3a). Mid-infrared photons can escape through this window into outer space, thus causing cooling. Most materials, including vegetation and commercial paints, have high emittance in the mid to far-infrared range, allowing for nighttime radiative cooling.[12,65]

Daytime radiative cooling is more challenging, as the thermal radiation process has to compete with heating via sunlight absorption. Recently, this challenge has been met by the development of spectrally selective surfaces that efficiently reflect sunlight and simultaneously emit efficiently in the mid-infrared. The refractive index engineering of multilayered structures consisting of hafnia (HfO_2) and silica (SiO_2) glasses resulted in daytime radiative cooling below the ambient temperature.[10,66,67] Glass-polymer hybrid metamaterials as well as metal-lined polymer films have also been developed for daytime radiative cooling.[13,14,16] Optically transparent polymers such as polyethylene and poly(methyl methacrylate) (PMMA) offer opportunities to create inexpensive, lightweight, and large-scale films for practical applications.

Wearable technologies can also be adapted to incorporate passive radiative cooling functionality. Since human skin is an almost ideal blackbody emitter in the infrared spectral range, fabrics that exhibit a transparency window in the same spectral range can help skin cool via the thermal radiation mechanism (Figure 3d).[68] Polyethylene is a polymer that exhibits uniquely low mid-infrared absorptance and high transmittance for thermal radiation from the skin. Polyethylene fabrics that combine visible opaqueness with infrared transparency have been theoretically predicted[15] and later demonstrated to achieve skin temperature reduction by 1–2°C relative to conventional textiles.[69–73] Visible opaqueness of the PE fabrics stems from

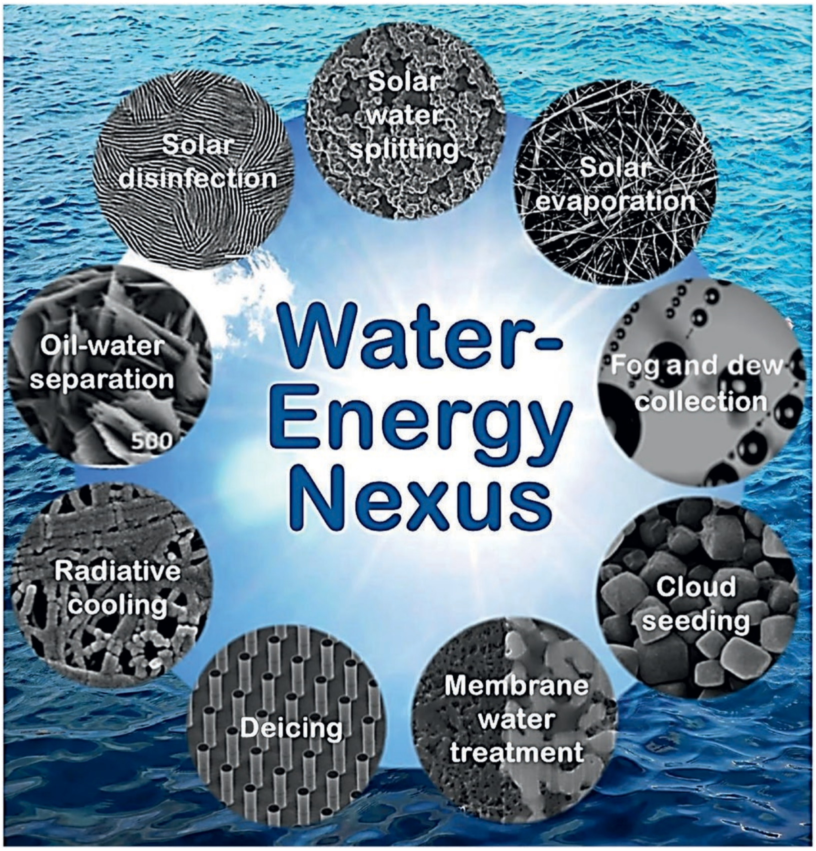

Figure 2. Examples of nano- and mesoscale materials developed to advance emerging technologies in the energy-water nexus. From the top, clockwise: solar water splitting (FeP/Ni_2P nanoparticles on a Ni foam),[20] solar evaporation (electrospun nylon/carbon fibers),[21] atmospheric water collection (dew drops on spider silk fibers),[22] cloud seeding (TiO_2 shell–NaCl core particles),[23] membrane water desalination and waste water treatment (nanoporous carbon composite membrane),[24] deicing of surfaces (silicon micropillars covered with Ti nanowires),[25] passive radiative cooling (nanoporous polyethylene film),[26] oil-water separation for treating produced water (nanostructured CuO mesh),[27] and solar microbial disinfection (vertically aligned MoS_2 nanofilms).[28]

light scattering by their internal microstructure comprised of either fibers or pores of 1–20 μm in size.

Water purification

Solar heat trapped by selective absorbers can be used for solar-driven water purification.[74] Vapor generation for water distillation in solar stills is an ancient technology[5] whose commercial adoption for large-scale applications has long been stymied by higher cost relative to membrane-based water purification techniques. However, passive solar technology offers an attractive solution for small-scale off-grid applications, especially in economically disadvantaged geographical locations or disaster zones. Recently, the interfacial solar vapor generation approach revived interest in solar distillation.[75–83]

Interfacial evaporation occurs on the surface of water and can be achieved by using a solar absorber floating on the water surface (**Figure 4**a).[40,84–86] To maintain high efficiency of the evaporation process, parasitic heat losses from the absorber should be minimized. These include optical loss (reflection) as well as thermal loss (heat conduction, convection, and radiation). To reduce all the losses, the absorber needs to be engineered to provide not only spectral selectivity, but also low thermal conductivity for vertical heat localization; a porous microstructure with high wettability for water transport; thermal, humidity and chemical stability; and opportunities for low-cost and scalable fabrication.

After demonstrations of the concept of heat localization for interfacial solar evaporation in high concentration plasmonic opto-nanofluids (i.e., suspensions of silica-core gold-coated nanoshells in water) and floating porous carbon foam absorbers,[75,76,87] many solar still designs and materials were reported. These included noble-metal nanospheres, nanoshells and nanorods,[55,78,81,88–92] less expensive carbon-based black absorbers,[21,43,93–95] and other exotic and nature-inspired materials, including paper, carbonized wood, leaves, and mushrooms.[79,96–98] For example, the structure of mushrooms offers a restricted vertical water pathway, which was utilized in the development of efficient solar evaporators based on natural carbonized mushrooms (Figure 4b).[85] High-temperature solar steam is of special interest for solar sterilization of food, waste, or medical equipment in off-grid locations,[99] and can typically only be achieved under concentrated sunlight and in pressurized systems. However, lateral thermal concentration[86] (Figure 4c) can increase vapor temperature up to the water boiling point by enlarging the ratio of solar absorption area to the evaporation area. Even higher steam temperatures can be reached in contactless solar stills, where a porous solar absorber is separated from the water surface by an air gap; it heats the water and the water vapor radiatively by emitting infrared photons.[100]

Overall, passive solar-thermal desalination has high potential for applications in decentralized water purification and zero-liquid discharge desalination, especially for high-concentration brine treatment that presents significant challenges for membrane-based filtration technologies.[101–103] Solar stills can be used for recycling valuable chemicals dissolved in brine and also produce water, and in combination with power generators[104] or solar-fuel generation systems,[80] they show great promise for urgent survival needs in areas with both water and energy shortages. To avoid fouling of floating solar still materials with salts left behind by the evaporation process, optimum combinations of hydrophilic wicking and hydrophobic insulating materials have been proposed (Figure 4d).[40,94]

Owing to many improvements in materials and design strategies, single-stage solar still technology is gradually approaching the production rate of mature filtration-based

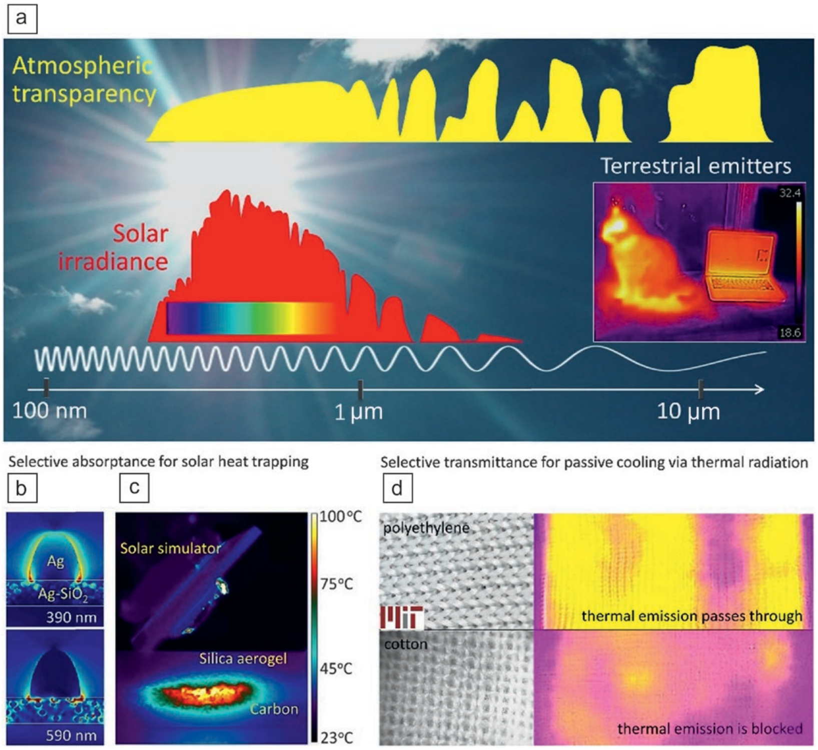

Figure 3. (a) Wavelength spectra of solar radiation (red) and atmospheric transparency (yellow). Terrestrial objects emit thermal radiation in the mid to far-infrared spectral range, which overlaps with the transparency window in the atmospheric spectrum, allowing for their passive cooling via radiation into the ultra-cold of outer space. (b) Local electromagnetic field intensity distribution at two separate wavelengths within the visible spectrum in a broadband solar absorber that combines thin-film interference and localized surface plasmon resonance effects in an Ag-SiO_2 nanocomposite structure.[57] (c) Local temperature distribution in the internally hot, externally cool solar absorber utilizing carbon foam as the blackbody absorber and a transparent silica aerogel[60] as thermal insulation material. (d) Optical (left) and infrared (right) images of a human hand covered with wearable fabrics, which are either blocking infrared emission from the skin (cotton, bottom) or allowing it to pass through (polyethylene, top).[68]

technologies (40–400 L/m²/day for seawater filtration), with a solar vaporization rate of 18–23 L/m²/day recently demonstrated under natural sunlight with a hierarchically nanostructured gel based on poly(vinyl alcohol) (PVA) and polypyrrole (PPy).[105] This high evaporation rate exceeds the photothermal efficiency limit, indicating that the phase-change enthalpy of water in nanoscale-confined space can be reduced, which is of both fundamental and applied importance.

The efficiency of the solar evaporation process can also be increased by environmental energy harvesting[82] and radiation loss recycling[106] strategies, as well as strategies to recover the latent heat of water vaporization, which is typically released into the environment once the vapor condenses in the fresh water collector.[107,108] A multistage solar still has been recently demonstrated, which recovers and reuses the latent heat several times prior to its release to the environment at lower temperature.[109] This still enjoys both advantages of thermal-based desalination and membrane-based filtration processes, and uses commercial spectrally selective coating (TiNOX) for solar absorption as well as polyethylene films for thermal insulation. Such a multistage system yields a large-scale purified water production rate of 72 L/m²/day, which is one magnitude higher than that achievable with single-stage solar stills.

Atmospheric water extraction

The atmosphere holds 12,900 billion tons of fresh water, equivalent to ~10% of the water in all of the lakes and six times the water in all rivers on Earth.[110] Harvestable atmospheric water, including water vapor and water droplets in fog, is present even in very dry desert regions.[110] Atmospheric water harvesting is emerging as an alternative approach for arid regions, landlocked, and remote communities.[111] Fog harvesting is the most ancient way of collecting air water, which has been used by plants, animals, and humans worldwide to harvest fresh water. Many modern nanostructured materials used in fog harvesting actually mimic biological systems of plants and insects.[112–116] However, fog harvesting necessitates consistently high (close to 100%) relative humidity (RH) in air, which makes it a viable solution only in some locations.[117,118] In regions with fresh water scarcity, harvesting water vapor from air is a more meaningful approach.[119]

Active refrigeration is currently the most popular way to extract water from the atmosphere.[120,121] The method uses an engineered cold surface to cool the adjacent air mass below the dew point to produce water droplets via condensation.[17,18,121,122] A sorption-based approach for atmospheric water vapor harvesting is also gaining popularity (**Figure 5**), in which a water sorbent, such as metal–organic framework (MOF), anhydrate salts, deliquescent salts, is used to harvest water vapor from air, and it is then heated with assistance from photothermal material to release and subsequently condense the water.[122–125] Effective photothermal materials, such as carbon nanotubes, carbon black particles, and graphene, have been utilized to directly tap sunlight to drive the water vapor release out of the water vapor sorbents.[105] The solar-photothermal process along with an effective water vapor sorbent has recently delivered fully solar energy-driven autonomous atmospheric water generator devices.[122,123,126]

An efficient vapor sorbent should be capable of absorbing large amounts of water, even from air with reasonably low RH, and releasing most of the water at a relatively low temperature (60–80°C) achieved under sunlight illumination.[76,127,128] Conventional desiccants, such as silica gel, zeolite, and activated alumina have a wide water vapor sorption window, but require high temperatures (>160°C) to efficiently release most of the captured water.[129–131] Recently, new material candidates have emerged that are capable of operation under sunlight.

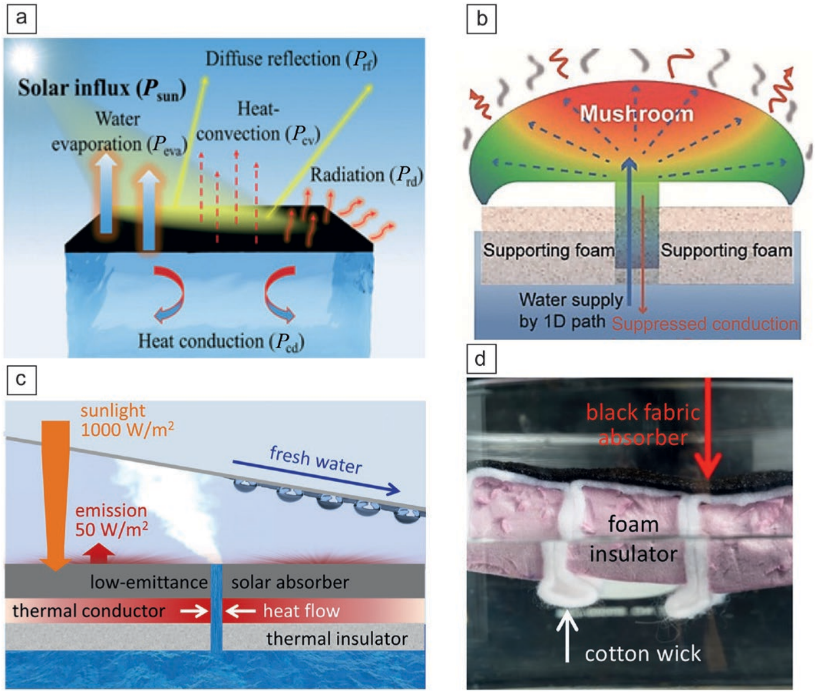

Figure 4. (a) Thermodynamic processes and energy balance in a floating solar still.[84] (b, c) Thermal management and water path design strategies can increase solar still efficiency. (b) Vertical thermal isolation in mushroom structures reduces thermal losses.[85] (c) Lateral thermal concentration in perforated floating stills enables water boiling under illumination by sunlight without any external optical concentrators.[86] (d) Optimizing the ratio of wicking and insulating surfaces mitigates effects of salt fouling and yields self-cleaning solar stills.[40]

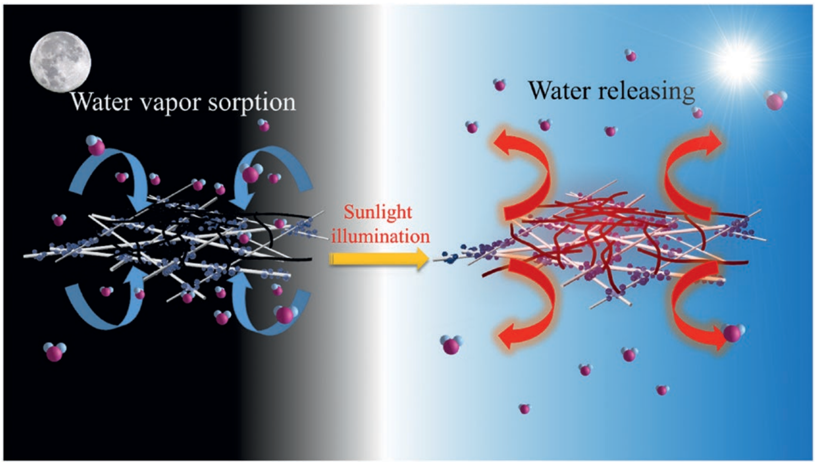

Figure 5. Schematics of the working principle of an atmospheric water generator,[126] based on the use of water sorbent materials such as metal–organic frameworks, anhydrate salts, or deliquescent salts.

These include MOFs such as $Zr_6O_4(OH)_4(fumarate)_6$,[122,123] anhydrous and hydrated salt couples ($CuCl_2$, $CuSO_4$ and $MgSO_4$),[126] and hydrogels.[132] It is expected that other sorbent materials will emerge in the near future with large water sorption capacities and easy water release. As research on photothermal conversion materials progresses, higher temperatures may be produced under natural sunlight, which would broaden the water sorbent materials pool.

Conclusion

As new technologies for water-energy nexus applications are developed and mature, they will inspire developments of new materials and application areas. Materials for daytime radiative cooling that help reduce the amount of energy needed for cooling buildings also find use in atmospheric water capture and dew collection.[16,18] On the other hand, light and heat trapping/spreading concepts and composite materials developed for solar water desalination technologies are now being adapted to engineer ice-phobic surfaces that use solar energy to prevent and mitigate ice formation.[133,134] New composite material systems are emerging to replace the commonly used table salt in cloud-seeding applications.[23,135,136] Many nanostructured materials used to address the challenges in the water-energy nexus continue to draw inspiration from existing natural solutions to engineering spectral selectivity, water wicking, vapor harvesting, and other functionalities.[71,79,96,97,113,137–144] Many challenges in materials engineering still remain, with the focus shifting to passive solar-driven operation, self-cleaning capabilities, and recyclability.[40,96,145]

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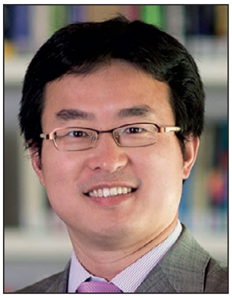
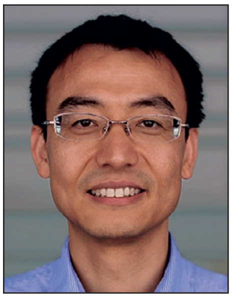
Svetlana V. Boriskina is a research scientist in the Department of Mechanical Engineering at the Massachusetts Institute of Technology. She received her PhD degree in physics and mathematics from Kharkiv National University, Ukraine. She previously worked as a research fellow at The University of Nottingham, UK, and Boston University. Her research focuses on the development of smart fabrics for thermal comfort, new metamaterials to manipulate light in unusual ways, and solar-harvesting platforms to provide clean energy and fresh water to off-grid and disaster-stricken communities. Boriskina has authored 110 publications, served as the principal investigator (PI) or co-PI on multiple US Department of Defense, US Department of Energy, and NATO-funded projects, and holds many patents on sensor, energy-conversion, and desalination systems. She is currently a director-at-large at The Optical Society, and an associate editor of *Optics Express* and the *Journal of Optics*. Boriskina can be reached by email at sborisk@mit.edu.

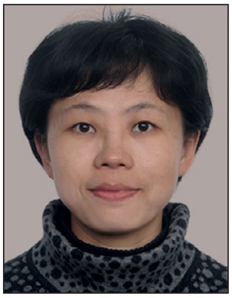
Aikifa Raza is a research scientist in the Department of Mechanical and Materials Engineering of the Masdar Institute, Khalifa University of Science and Technology, United Arab Emirates. Her research interests include nano-/microfabrication and characterization for solar-thermal applications and the characterization of interfacial adhesive forces between different materials using the quantum nanomechanical atomic force microscopic approach. She has published more than 30 peer-reviewed papers and five book chapters. Raza can be reached by email at aikifa.raza@ku.ac.ae.



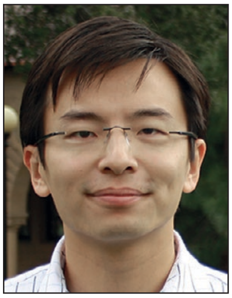
TieJun (TJ) Zhang is an associate professor of mechanical and materials engineering at the Masdar Institute, Khalifa University of Science and Technology, United Arab Emirates (UAE). He was a visiting assistant professor at the Massachusetts Institute of Technology, and a postdoctoral research associate at the Rensselaer Polytechnic Institute. He received the UAE National Research Foundation University-Industry Research Collaboration Award, and served as the PI of multiple research projects on energy and micro/nanotechnologies. He has authored more than 130 publications on phase-change heat transfer and microfluidics, nanomaterials synthesis and advanced microfabrication, solar-power generation and refrigeration cooling, subsurface multiphase flow and water treatment, and energy process dynamics and control. He is a member of The American Society of Mechanical Engineers (ASME) NanoEngineering for Energy and Sustainability Steering Committee and ASME Heat Transfer Division K18 Technical Committee. Zhang can be reached by email at tiejun.zhang@ku.ac.ae.



Peng Wang is an associate professor of environmental science and engineering at King Abdullah University of Science and Technology (KAUST), Saudi Arabia. He is affiliated with the Water Desalination and Reuse Center and KAUST Solar Center. His research interests include nano-photothermal material-assisted solar desalination, atmospheric water harvesting, smart materials-enabled solar cooling, oil/water separation, and energy harvesting. He has published more than 70 papers in prestigious journals and three academic books, and is on the advisory board of *Advanced Sustainable Systems*. Wang can be reached by email at peng.wang@kaust.edu.sa.



Lin Zhou is an associate professor of quantum electronics and optics engineering in the College of Engineering and Applied Sciences at Nanjing University, China. She is also a research scientist at Columbia University. Her research interests lie in nanophotonics, plasmonics, and related energy-conversion systems. Her current research focuses on nanophotonics design of plasmonic microstructures for solar-thermal conversion, and emerging materials for solar absorbers, solar desalination, and solar thermo-photovoltaics. She has published more than 40 peer-reviewed papers and one book chapter. Zhou can be reached by email at linzhou@nju.edu.cn.



Jia Zhu is a professor in the College of Engineering and Applied Sciences at Nanjing University, China. He received his MS and PhD degrees in electrical engineering from Stanford University, and worked as a postdoctoral fellow at the University of California, Berkeley, and Lawrence Berkeley National Laboratory. His scientific research interests lie in the areas of nanomaterials, nanophotonics, and nanoscale heat transfer. Zhu has received several prestigious awards, including the OSA Young Investigator Award (2017), Dupont Young Professor Award (2016), *MIT Technology Review* TR35 Award (2016), and the Recruitment Program of Global Experts (2014). He has published more than 60 papers and delivered more than 40 keynote/invited lectures at leading research institutions, international conferences, and the US Department of Energy. He is an advisory board member of *Molecular Systems Design & Engineering*. Zhu can be reached by email at jiazhu@nju.edu.cn.