Salt-Resistive Photothermal Materials and Microstructures for Interfacial Solar Desalination

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Solar interfacial evaporation, featured by high energy transfer efficiency, low cost, and environmental compatibility, has been widely regarded as a promising technology for solar desalination. However, the interplay between energy transfer and water transport in the same channels suggests that the tradeoff between high efficiency and long-term stability inherently exists in conventional photothermal nanomaterials. We summarize state-of-the-art research on various anti-salt clogging photothermal microstructures as long-term stable interfacial solar evaporators for solar desalination. The review starts with an overview of the current status and the fundamental limit of photothermal materials for solar desalination. Four representative strategies are analyzed in detail with the most recent experimental demonstrations, including fluid convection enhancement, surface wettability engineering, energy-mass-path decoupling, and surface chemistry engineering. Finally, this article focuses on the challenges in anti-salt clogging solar interfacial evaporators and potential point-of-use applications in the future.

Keywords: photothermal, desalination, solar interfacial evaporation, anti-salt clogging, structure design

INTRODUCTION

The shortage of freshwater resources has become one of the most severe global challenges nowadays (Shannon et al., 2008; Elimelech and Phillip, 2011; Cetrulo et al., 2019). To address the current situation of global water scarcity, widespread concerns have been garnered about freshwater extraction from seawater (Dobson et al., 2002; Gude, 2011). Solar desalination is an environment-friendly water treatment technology without the additional consumption of fossil energy (Kalogirou, 1997; Abdel-Rehim and Lasheen, 2005; Qiblawey and Banat, 2008). In recent years, a promising route, interfacial solar vapor generation, has been proposed and developed to promote the photothermal conversion efficiency of liquid-gas phase transition of water, dramatically improving vapor production (Tao et al., 2018; Zhou et al., 2019; Vaartstra et al., 2020). The performance of solar vapor generation can be significantly enhanced by floating the absorber or evaporator at the water-air interface to evaporate the water at a relatively localized photothermal area (the liquid/air interface), which is therefore named interfacial solar vapor generation (Ghasemi et al., 2014; Wang et al., 2014). The rapid development of solar water treatment technologies has thus been essentially improved.

However, most of the proposed interfacial solar evaporators have been more or less suffering from the rapid decay of energy transfer efficiency and poor stability during the long-term operation of solar desalination (Li et al., 2020; Zhang Q. et al., 2020). Therefore, it is vital to inhibit salt deposition
to maintain long-term solar vaporization. Traditional methods are rinsing and washing in the post-treatment process (Finnerty et al., 2017; Jin et al., 2018; Zhang et al., 2018; Xiao et al., 2019; Zhu et al., 2019). However, they introduced extra treatment costs and merely worked for washable and flexible membrane absorbers. In addition, by logically segregating the light-absorbing surface from the surface of salt precipitation, rationally designed absorbers can precisely monitor the position of salt precipitation to allow long-lasting, high-performance, and ZLD solar desalination (Shi et al., 2018; Zeng et al., 2019; Zhang et al., 2020b; Wu et al., 2020; Xia et al., 2020; Zhuang et al., 2020). However, the imperfections of the above methods are that the threat of salt accumulation on the absorber surface to light absorption and permeability can interrupt the generation of stable and high-efficiency steam in long-term desalination and highly concentrated brine.

Aiming to solve or alleviate the salt clogging issue, the researchers have developed a couple of effective strategies to develop stable solar desalination devices with anti-salt clogging properties. We evaluate the state-of-the-art solar interfacial desalination as shown in Figure 1. It illustrates that the reported anti-clogging mechanisms for solar interfacial systems can be categorized into four major groups: 1) fluid convection can dilute the formed high concentration brine in the absorbers during desalination; 2) Hydrophobic designs can prohibit the contact of salt ions with the solar absorber; 3) Thermal engineering by re-radiating infrared photons can entirely avoid fouling via the physical separation from the brine; 4) Donnan that can prevent ions upward movement by creating the double electrode layer.

**ENHANCED FLUID CONVECTION: MULTISCALE HIERARCHICAL STRUCTURES**

In the past years, various research groups have suggested that the primary issue that accounts for the salt accumulation is the emergence of the saturated salt solution on the solar absorber surface during the highly efficient interfacial solar desalination process. Therefore, it is of tremendous importance but rather challenging for rationally designing structures capable of high-flex ion diffusion. A variety of concepts have been proposed and demonstrated experimentally, including multi-scale precise manipulation of the structures of solar evaporators across the microscale to the macroscopic scale. One of the most representative strategies, reported by Chen group (Ni et al., 2018), is the regulation of micro/macro structures because of the rapid diffusion of ions through the micro/macro channels (Fang et al., 2019; He et al., 2019; Liu et al., 2019; Wang C. et al., 2020; Zhu et al., 2017). As shown in Figure 2A, in this salt-rejecting evaporator proposed by Chen et al., the hydrophilic white fabric is composed of microstructured pores and channels and artificially confined in macroscale narrow gaps among thermal insulation foams, which can finally wick the underlying water into the absorber layer. At the same time, the highly concentrated salt solution can be effectively diffused back into the remaining water. When the intriguing design integrated with a cost-effective polymer film condensation cover, the overall system can produce clean water at a rate of 2.5 L m⁻² per day at a total system cost of about $3 m⁻², which is sufficient to meet individual drinking requirements without energy framework while cheaper than conventional solar stills by order of magnitude, ideal for water-stressed and disaster-ridden populations with affordable drinking water. Similarly, inspired by banyan, a hierarchical evaporator consisting of an activated carbon-cotton fabric, a polyester pillar, and an expandable polyethylene foam was suggested by Zhang et al. (Zhang et al., 2020c). A banyan tree in nature grows with several aerial prop roots to meet the growth of plants, growing eventually into the soil for additional water availability. By modifying the amount of PPs during desalination, the suggested hierarchical evaporator was shown to exhibit anti-salt clogging ability.

In addition, macro-pores of solar absorbers can also be utilized as efficient water channels to prevent salt deposition through enhanced fluid convection. Porous wood-based solar evaporators were reported by the Hu group (Zhu et al., 2017; He et al., 2019) for effective and safe high-salinity water desalination. The outstanding antifouling characteristics are due to its distinctive porous bimodal and 3D interconnected microstructure. During desalination, the rapid diffusion and evaporation of water and the capillary pumping of micro-channels in the system lead to a rapid re-supply of surface vaporized brine to maintain consistent and rapid production of water vapor. Further research has shown that a self-regenerating solar evaporator with outstanding anti-
properties is recognized via a rationally designed virtual channel array in a natural wood substrate (Liu et al., 2018). Artificial polymer porous foams (Zhang et al., 2019a; Wang X. et al., 2020; Dong et al., 2020; He et al., 2020) with super-hydrophilic wettability have also been introduced. The sufficient water transport in these solar evaporation systems have been widely regarded to be beneficial to resolve the crystalline salt through enhancing fluid convection.

SURFACE WETTABILITY ENGINEERING: HETEROGENEOUS HYDROPHILICITY

By enhancing fluid convection, the anti-salt evaporators cannot maintain efficient evaporation out of high-salinity brine (over 10 wt%) because of the excessive salt solubility on the solar absorbers during desalination. Hence, the effective way to prevent salt deposition on the absorber is to blocks water molecules while allowing steam. It is also noteworthy that the hydrophobic surface of a solar absorber can effectively prevent water while blocking salt ions from penetrating into the absorber and thus water evaporation happens at the bottom of the absorber (Gao S. et al., 2019; Chen et al., 2020; Peng et al., 2021). The hydrophobic surface of solar absorbers has been gradually recognized as salt-rejective solar evaporators by a couple of groups (Kashyap et al., 2017).

As illustrated in Figure 2B, Xu et al. (Xu et al., 2018) indicate that safe and effective solar desalination can be facilitated by a sequential electrospinning flexible Janus absorber. The membrane can be divided into two primary parts—the hydrophobic upper levels for salt-resistance and the porous and hydrophilic lower level for water supply. Benefiting from Janus’ unique structure, solar absorption and water pumping are split into various layers with polymethylmethacrylate (PMMA) coating of the hydrophobic upper carbon black nanoparticles (CB) for light absorption and the lower polyacrylonitrile (PAN) hydrophilic layer for water pumping. As a result, salt can only be accumulated in the PAN hydrophilic layer and easily dissolved due to consistent water pumping. High efficiency and steady water generation (1.3 kg m-2 h-1, over 16 days) under one Sun is shown by the Janus absorber, which has not been obtained in many previous absorbers. Similar Janus cotton fabrics with salt-rejection properties may also be reported by Lai et al. (Gao T. et al., 2019). However, the absorbers mentioned above are in direct contact with the volume of water, resulting in heat dissipation through the water. The vertically oriented Janus
MXene aerogel with a hydrophobic upper layer and a hydrophilic lower layer was designed by Quan et al. (Zhang et al., 2019b). MXene, which has a theoretical light-to-heat conversion capability of 100 percent, can easily convert light to heat in combination with the Janus structure and protect the photothermal layer from direct bulk water interaction with the hydrophobic upper layer, thereby reducing heat loss and thus effectively inhibiting the crystallization of salt owing to its fast dissolution with continuous pumping water. Among most Janus absorbers, the hydrophobic upper layer of the absorber was generally generated by manipulating with a polymer solution, which may block the steam escape pathways. An innovative double-layer hydrophilic/hydrophobic nonporous structure was designed by Que et al. (Yang et al., 2018). A porous hydrophobic layer can withstand salt deposition and supply pathways for vapor evaporation. Water vapor is generated and then lost through the stomata on the upper epidermis in the natural water lily. The hydrophobic surface is the root cause of the self-cleaning property. Xu et al. modeled a water lily-inspired hierarchical structure composed of a bottom bracket and a top solar absorber (Xu et al., 2019). Unlike most conventional structures of salt rejection, there was a thin water film at the interface between the bottom supporter and the top hydrophobic absorber. This sandwich structure plays a vital role in achieving safe and efficient high-concentration brine evaporation in this design. The formed salt particles or high salt solution gradually diffused to the bulk brine along the one-dimensional channel rather than accumulating in the absorber during desalination.

**SURFACE CHEMISTRY ENGINEERING: DONNAN EFFECT FOR PRE-INTERCALATION OF SALT IONS**

As discussed in the previous part, the deposition of salt is mainly due to the increasing concentration of salt on the top surface of the solar absorber. The regulation of the local salt concentration in the absorbers is an effective and desirable way to avoid salt deposition. The salt ion has positive/negative charges on the top surface of the solar absorber. Hence, the key is to regulate the number of salt ions in the absorbers according to the boundary-layer differential equation for mass transfer (Pantoja et al., 2015). Donnan effect can prevent ions upward movement by creating a double electrode layer due to electric neutrality, which can be a good way for enhanced anti-fouling performance (Chang and Kaplan, 1977; Cumbal and SenGupta, 2005; Galama et al., 2013; Ma et al., 2020).

Depending on the pH of the polyamide NF membrane, the rejection behavior of sodium cation-containing ternary ion solutions (Na+) and two monovalent anions has been consistently examined by Razi Epsstein et al. (Epsstein et al., 2018). The Donnan (charge) exclusion mechanism in the NF is more likely to affect anion with a smaller ion radius and a relatively high charge density. Membranes based on graphene oxide (GO)-based suffer from either low water flow or low ion rejection when employed for desalination. Chengzhi Hu et al. (Hu et al., 2018) successfully created an electroconductive three-dimensional hybrid membrane by employing reduced GO and carbon nanotubes (GCN) and showed significant ability to overcome the tradeoff between selectivity and permeability when performed concurrently as a filer membrane and electrode. In addition to developing various water transport channels to facilitate permeability, the intercalation of carbon nanotubes (CNTs) in the reduced GO matrix has also improved the active adsorption sites for salt ions, contributing to an improved Donnan effect and extraordinary salt rejection. An exceptional NaCl rejection of 71 percent was accomplished by the optimized GCN (containing 15 percent CNTs, three times higher than without bias. As shown in Figure 2D, Zhu et al. recently described a hierarchically designed evaporator with salt-resistant ability based on the Donnan effect (Zhao et al., 2021). Due to the Donnan distribution equilibrium, this structure can
minimize the number of salt ions in the absorber while supplying water. This hierarchically designed evaporator is shown by high efficiency (80%) and steady water generation under one Sun in high-salinity brine (15 wt% NaCl).

CONCLUSIONS AND OUTLOOK

Interfacial solar desalination has been intensely pursued as the most effective method for obtaining cleaner freshwater, attributing to an intrinsic low cost, high conversion efficiency, and eco-friendliness. However, the accumulated salt on the absorbers during desalination blocks continues the solar energy input and the vapor escape channels, leading to a significant decrease in the steam yield. In response to this problem, tremendous efforts have been dedicated to developing solar interfacial evaporators with an antifouling performance for long-term and stable desalination. This mini review summarized different solutions for inhibiting the salt deposition on absorbers’ surfaces, including enhancing fluid convection, surface wettability engineering, decoupling energy-mass transport paths, and surface chemistry engineering. These researches are of paramount importance in improving our insight into the development of stable and continuous desalination.

There is still a wide gap between the current strategy and the practical uses due to the complicated process of crystalline salts. Therefore, the deep study still needs more effort in future studies. 1) The yield of freshwater is critical for practical application in the solar interfacial desalination process. However, most of the previous devices still focus on the steam yields rather than the water yield to date. Therefore, the high yield of freshwater from seawater is still a fundamental challenge in solar interfacial desalination. 2) Based on the deep understanding of the principles of water transport, salt crystallization, evaporation, continuous steam production, and solid salts harvesting were proposed (Xia et al., 2019; Shao et al., 2020; Xia et al., 2020; Xu et al., 2021), which provides a new direction in further research. Hence, the collection of salt or chemicals of economic value should be consecrated deserves some attention in the process of solar interfacial desalination. 3) Regarding the current solar interfacial desalination devices, the main obstacle to solar interfacial desalination in practical uses is commercial-scale manufacturing.

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All authors listed have made substantial, direct, and intellectual contribution to the work and approved it for publication.

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