Designing a bioinspired synthetic tree by unidirectional freezing for simultaneous solar steam generation and salt collection

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Abstract
Solar steam generation with thermal localization was recently proposed for highly efficient solar-thermal desalination. However, to achieve high steam productivity with long term stability remains a critical challenge due to salt accumulation at the evaporation surface. Here, we designed a T-shaped synthetic tree that could simultaneously achieve high steam productivity and salt collection with the structure characteristics of interfacial thermal evaporation, ambient energy harvesting and edge-preferential crystallizing. Under 1 sun, the synthetic tree exhibited a steady water evaporation rate of 2.03 kg m$^{-2}$ hours$^{-1}$ over 60 hours, achieving solar thermal efficiency of 75%. Salt was continuously rejected at the edge of the evaporator with a steady collection rate of 59.879 g m$^{-2}$ hours$^{-1}$, which did not affect water evaporation. This new design principle to simultaneously harvest water and salt provides a new avenue for solar energy utilization.

KEYWORDS
bioinspired synthetic tree, salt collection, solar steam generation

1 | INTRODUCTION

Freshwater scarcity is threatening billions of people worldwide.$^1$ Oceans cover 3/4 of the surface of the earth and provide water and mineral salt resources. To alleviate freshwater scarcity, seawater desalination is a promising solution. Among various desalination technologies, such as reverse osmosis and ion exchange, the solar still is distinguishable due to its low energy consumption and little impairment on natural freshwater ecosystems.$^2,^3$ To promote practical application of the solar still, it has been long developed from bottom heating model, bulk heating model to interfacial heating model with increasing solar efficiency and reducing cost.$^3$–$^8$ In the interfacial heating model, solar energy is localized at...
the evaporation surface by high light absorption and low thermal conduction to bulk water using a floating structure.9 Attention has mainly focused on high absorption in the solar spectrum, low thermal loss from the evaporation surface and sufficient water supply for evaporation.6,9–11 Various absorbers, such as carbon-based materials, conjugated polymers, semiconductors, and plasmonic nanomaterials, have been designed to float on the surface of water.2,12–15 However, to reduce heat loss in the form of heat conduction to bulk water, water is usually transported to the evaporation surface via capillary channels, where salt accumulation easily occurs.16–20 The accumulated salt can severely reduce the adsorption efficiency, clog the water path, and decrease the evaporation area. As a result, solar steam generation process will be stopped without a sufficient water supply. To address this issue, innovative strategies have been proposed.21 For example, the accumulated solid salts can be removed by a supererogatory washing process.22,23 Alternatively, water transport channel has been designed to transport salt back to bulk water under a concentration gradient.17,19,24–26 However, considering the value of mineral resources in seawater, it is better to simultaneously harvest steam and salt during the solar-thermal utilization process.18,27

In this manuscript, we designed a bioinspired synthetic tree to simultaneously and efficiently generate solar steam and collect salt. A polyvinyl alcohol (PVA) synthetic tree with free-standing T-shaped asymmetric structure was designed. Since the edge of the T-shaped structure is farthest from bulk water, the salt concentration is highest at the edge of the evaporation disk with water evaporation and salt will preferentially crystallize at the edge. Thus operation of the solar still will not be interrupted by salt accumulation and less brine will flow back to seawater, leading to little impairment in the natural ecosystems. Meanwhile, this T-shaped structure can achieve interfacial evaporation and exploit environmental energy. Under 1 sun, the synthetic tree achieved a water evaporation rate of 2.03 kg m\(^{-2}\) hours\(^{-1}\) and a salt rejection rate of 59.879 g m\(^{-2}\) hours\(^{-1}\), with the solar thermal efficiency of 75%. The synthetic tree could steadily operate over 60 hours with continuous salt crystallization, proving its long-term durability. This result provides a novel avenue for solar energy and ambient utilization, and demonstrates the potential of the synthetic tree for simultaneous salt collection and seawater desalination.

### 2 | RESULTS AND DISCUSSION

A natural vascular plant transports tons of water from soil to air per day using a specialized phloem network powered by sunlight. This continuous water transport is efficiently achieved with reduced pressure in the leaf because of water evaporation.28,29 Herein, a free-standing PVA-based bioinspired synthetic tree with T-shaped asymmetric structure was designed with a unidirectional freezing method. The PVA matrix has excellent mechanical strength, and can support a 200 g weight (Figure S1). After surface polymerization of polypyrrole (PPy) nanoparticles, the white PVA matrix completely turned to black (Figure 1A). The micro- and nanochannels in the bioinspired synthetic tree ensured strong water absorptivity and low thermal conductivity. Under solar light irradiation, the synthetic tree spontaneously pumped water via the reduced pressure in the inner channels to the heating surface, and generated high-temperature steam (Figure 1B).5,30 Thermal convection was inhibited in these channels, so heat was localized at the evaporation surface and the solar-heat conversion was efficiently achieved.13,31,32 During the solar steam generation, the salt solution is subjected to an advection-diffusion process (Figure 1C). Due to the high aspect ratio of T-shaped structure, the salt concentration in the upper disk increases with the distance from the center. Thus if the upper disk is sufficiently large and the convection process surpasses the diffusion process, the salt solution in the disk will be saturated, and salt will preferentially crystallize at the edge of the disk. The crystallized salt gradually accumulates and falls out under the effect of gravity if the evaporation disk has an appropriate diameter. Finally, salt crystallization and water evaporation are simultaneously achieved under the sun flux.

The porous PVA matrix was prepared by unidirectional freezing and low-temperature curing of presdesigned polymeric matrices.33,34 First, PVA solution (containing crosslinking agent) was poured into a preassigned T-shaped vessel. Then unidirectional freezing was used, in which the temperature difference was applied using liquid N\(_2\), and unidirectional ice crystals induced a cellular structure in the PVA liquid precursors (Figure 2A).34 This hierarchical cellular structure was fixed after PVA precursors curing at −20°C and freeze-drying. Then PPy was surface-polymerized to enhance the light absorption of this synthetic tree. The hierarchical cellular structure was confirmed by scanning electron microscope (SEM), which showed unique fishbone structures with interconnected channels (Figure 2B-D). The PVA matrix consisted of parallel hollow tubes with a pore size of ~50 μm and a mesoporous wall with a thickness of 5 to 10 μm. N\(_2\) adsorption/desorption isotherms were used to characterize the porosity of the PVA-based synthetic tree (Figure 2F). The sample had a Type III isotherm with no obvious saturated adsorption platform, indicating that the pore size distribution (inset) was irregular.35 PPy particle with a diameter approximately
400 nm were successfully deposited on the surface of the PVA matrix as shown in Figure 2E and Figure S2. The chemical composition of the PVA/PPy sponge was analyzed by Fourier transform infrared (FTIR) spectroscopy (Figure 2G). In the PVA spectrum, the peaks at 1097 cm$^{-1}$ could be attributed to C–O stretching, which is a characteristic peak of PVA. The PPy spectrum had absorption signals at 1544 cm$^{-1}$ and 1035 cm$^{-1}$, which correspond to the in-ring stretching of C=C bonds in the pyrrole rings and in plane deformation of N–H bonds, respectively. All the characteristic peaks of PVA and PPy were found in the FTIR spectra of the PVA/PPy composite without shifts, confirming the presence of PPy in the PVA matrix.

The high absorption in the solar spectrum, thermal insulation to bulk water, and presence of hydrophilic and interconnected pores for water supply are essential to achieve heat localization in solar-thermal conversion. To quantitatively evaluate the light absorption of synthetic tree, we measured the ultraviolet-vis (UV-vis) near-infrared (NIR) spectra (wavelengths 300-2500 nm, Figure 3A). The original PVA was white and had a poor light absorption ability. After the surface-polymerization of PPy particles, the light absorption ability was obviously increased with the over-all light absorbance of 97%.

Water transport in synthetic tree was enabled by capillary pumping with the hierarchical cellular structure.

**FIGURE 1** Schematic of the synthetic tree for solar steam generation and salt collection. A, Photographs of the T-shaped PVA sponge and PVA/PPy composite with the channel structure. The disk is ~2.8 cm in diameter and 3 mm in thickness. The column is ~0.8 cm in diameter and 4 cm in height. B, Schematic illustration of the bioinspired synthetic tree for solar steam generation and salt collection. The disk is 3 cm above the water surface. C, Illustration of the water and salt transport system.
The water transport ability of synthetic tree was represented by swelling of the PVA matrix from the half-saturated state to the fully saturated state (Figure 3B). As expected, the PVA matrix had an excellent water transport ability (-Figure S3). The water transport rate was as high as $1.2 \times 10^{-4}$ m s$^{-1}$ in the half-saturated state and gradually decreased. Because of the inherent asymmetry of the oriented pore structure, the water transport rate in the parallel direction of the pore was slightly larger than that in the vertical direction. It took approximately 15 minutes to reach the saturated state from the half saturated state in both directions of the synthetic tree.

The thermal conductivity of PVA matrix is shown in the Figure 3C. The dry PVA matrix had a low thermal conductivity of 0.16 W m$^{-1}$ K$^{-1}$ because of its porous structure. When the PVA matrix was filled with water, the thermal conductivity obviously increased to 0.57 W m$^{-1}$ K$^{-1}$, indicating that thermal convection was inhibited in the water channels and favorable for heat localization.$^{12}$

Because of the asymmetric T-shaped structure of the bionic synthetic tree, the salt concentration distribution is uneven due to water evaporation. We used the COMSOL Multiphysics software to perform simulations to...
better understand the advection and diffusion of salt in the mass transfer process (details are provided in the ESI). In the solar steam generation process, the temperature field, velocity field, and salt concentration distribution are shown in Figure 3D. The simulation of the steady-state temperature distribution predicted that solar-heat was localized at the disk of the T-shaped synthetic tree at the highest temperature approximately 35°C. The velocity distribution indicated that water quickly transported through the column of the T-shaped synthetic tree against surface water loss. Salt was transferred with evaporated water, and a salt gradient formed, in which the outer part of the disk had a higher salt concentration. This result was confirmed by experimental measurements, as shown in Figure 3E, and a salt ring with a certain diameter formed in the bionic synthetic tree with water evaporation, instead of homogeneous salt crystallization. Hereafter, the diameter of the salt ring is intended to be the diameter of the T-shaped bionic synthetic tree for simultaneous solar steam generation and salt collection.

A bionic synthetic tree with a certain diameter was then used for solar steam generation and salt collection. Because of the 3D structure of synthetic tree, the evaporation area is larger than the illuminated area. Synthetic tree with is a side sealed (Synthetic tree I) is presented here, in which the evaporation area and illuminated area is same (Figure S4). The temperature and mass change under 1 sun of the synthetic tree I and synthetic tree II (side unsealed) are presented in Figure 4A,B respectively. Under a solar intensity of 1 kW m\(^{-2}\), the steady-state surface temperatures of bulk water and synthetic tree I were 28°C and 43°C, respectively, and the evaporation rates were 0.26 kg m\(^{-2}\) hours\(^{-1}\) and 1.09 kg m\(^{-2}\) hours\(^{-1}\). The thermal efficiency increased from 17.7% to 75%. Thus, the synthetic tree could effectively convert solar flux to heat and achieve the interfacial evaporation model. For synthetic tree II, the steady-state surface temperature and evaporation rate were 37°C and 2.03 kg m\(^{-2}\) hours\(^{-1}\), respectively, because its evaporation area is doubled compared to that of synthetic tree I and ambient heat is harvested.\(^{36}\) The temperature distribution in the infrared thermal image also confirms that solar-heat was localized at the evaporation interface, and that the ambient environmental energy enhanced water evaporation (Figure 4C; Figure S5). Because synthetic I and synthetic II has same structure for thermal localization, the solar-thermal efficiency of synthetic II is considered to be the same with synthetic I (Table S1). The salt concentration distribution of the synthetic tree under 1 sun was investigated by cutting the evaporation disk into small blocks.
along its radial direction. As shown in Figure 4D, the salt mass fraction increased from the center to the edge of the disk, consistent with the COMSOL simulation results (Figure 3D). Water evaporation and salt collection were performed for over 60 hours to demonstrate the stability of the synthetic tree, as shown in Figure 4E,F. Over 60 hours, the evaporation rate was steady, since salt crystallization only occurred at the edge of the evaporation disk. And PPy particles are still adhered on PVA sponge for its strong bond strength with PVA (Figure S6).
salt collection. The thermal localization, ambient energy harvesting and asymmetric structure of the bioinspired synthetic tree assure the high productivity of this system. Since salt was rejected at the edge of the evaporator, the system could steadily run for over 60 hours with a water evaporation rate of 2.03 kg m$^{-2}$ hours$^{-1}$ and a salt rejection rate of 59.879 g m$^{-2}$ hours$^{-1}$ under 1 sun. The successful application of an asymmetric structure in the solar-driven desalination system shows its promise for by-product recovery for which both a high flux and good antifouling ability are required.

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3 | CONCLUSION

In conclusion, we present a T-shaped bioinspired synthetic tree for simultaneous solar steam generation and...
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SUPPORTING INFORMATION
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