

Supporting Information

Synergistic utilization of *Vaccinium bracteatum* *Thunb.* leaves for coupled solar evaporation and selective lithium extraction from seawater

Zhiyu Chen, Junkai Gao, Yushan Zhang, Xinghai Liu, Yan Chen*

School of Naval Architecture and Maritime, Zhejiang Ocean University, Zhoushan
316022, China

* Corresponding author. Tel.: +86 580 2550623. E-mail: chenyan@zjou.edu.cn

1. Test methods

1.1. Characterization

Surface functional groups and elemental states were examined by Fourier transform infrared spectroscopy (VECTOR 22, Bruker, Germany) and X-ray photoelectron spectroscopy (ESCALAB 250, Thermo VG, USA), respectively. Wettability was evaluated by static water contact angle measurements performed on a contact-angle goniometer (Chengdu Dingsheng Instrument Co., Ltd., China). The microstructural features and surface topography of the samples were further observed using a scanning electron microscope (Quanta FG-250, FEI, USA). The reflectance and transmittance were measured using a UV–Vis–NIR spectrophotometer (UV-3600i Plus, Shimadzu, Japan) over the wavelength range of 300–2500 nm. The metal-ion concentrations in the evaporation tests were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo, USA), and the lithium-ion concentrations before and after adsorption were measured by flame atomic absorption spectrometry (FAAS).

1.2 Evaporation measurement

In the evaporation experiments, the evaporator was thermally insulated with polystyrene foam and suspended in a beaker containing distilled water. The solar-driven steam generation performance was tested under a solar simulator (PLS-SXE 300, Beijing Perfectlight), and the incident spectrum was calibrated using an AM 1.5 optical filter. The illumination intensity was first calibrated to the desired level with a solar power meter (PL-MW 2000, Beijing Perfectlight). During the experiment, water loss

was continuously tracked by an analytical microbalance (0.1 mg readability). In parallel, the spatial evolution of the sample-surface temperature was captured using an infrared thermography camera (FLUKE TiS 20⁺).

The evaporation performance was quantified from the time-resolved decrease in water mass in the evaporation setup. On this basis, both the evaporation flux and the corresponding efficiency were calculated. The evaporation flux, denoted as m (kg/(m²·h)), was computed using the following expression:

$$m = \frac{\Delta m}{S \cdot \Delta t}$$

In this equation, S (m²) represents the effective evaporation area of the device, Δt (h) is the elapsed evaporation duration, and Δm (kg) corresponds to the water mass decrease over the same period.

The photothermal evaporation efficiency, denoted as η , was then evaluated according to the expression below:

$$\eta = \frac{m h_{lv}}{C_{opt} P_0}$$

Here, m (kg/(m²·h)) is the evaporation rate, h_{lv} (J/kg) is the total enthalpy of vaporisation, including sensible heat and phase-change enthalpy, and C_{opt} (W/m) denotes the solar irradiance. Accordingly, h_{lv} was determined from comparative evaporation tests of pure water and the evaporator conducted for the same duration under matched ambient temperature and relative humidity.

$$h_{lv, evaporator} \times m_{evaporator} = h_{lv, water} \times m_{water}$$

1.3 Adsorption performance test

1.3.1 Lithium Ion Adsorption Experiments

Lithium-ion solutions with various starting concentrations were prepared by dissolving lithium chloride in distilled water. For each run, the sample was contacted with 100 mL of the LiCl solution and agitated at 150 rpm for 12 h at the designated temperature using an incubator shaker (Crystal ISRDS6). The suspension was then passed through a 0.22 μm microporous membrane to remove the solid phase, and the residual Li^+ concentration in the filtrate was quantified by flame atomic absorption spectrometry (PerkinElmer, USA). All experiments were performed in triplicate to ensure the reliability of the results. The lithium adsorption capacity (q_e) and removal efficiency were calculated using the following equations:

$$q_e = (C_0 - C_e) \times \frac{V}{m}$$

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\%$$

In the above expressions, V (L) denotes the volume of the solution and m (g) is the mass of the adsorbent used. C_0 and C_e (mg/L) correspond to the Li^+ concentrations at the start of adsorption and at equilibrium, respectively.

1.3.2. Adsorption Isotherm Measurements

For isotherm evaluation, LiCl solutions (100 mL) were prepared with a series of initial Li^+ concentrations of 25, 50, 75, 100, 150, 200, 300, 400, 500, and 600 mg/L, and the pH was adjusted to 12. The adsorbent was then contacted with each solution and agitated at 150 rpm in a thermostatic shaker maintained at 25 $^{\circ}\text{C}$ for 12 h to reach

equilibrium. Subsequently, the remaining Li^+ concentration in the supernatant/filtrate was quantified by flame atomic absorption spectrometry (PerkinElmer, USA).

1.3.3. Adsorption kinetics

For kinetic measurements, PVV@VLJ-LIS was contacted with 100 mL of LiCl solution adjusted to pH 12. The mixture was agitated in a thermostated orbital shaker at 25 °C and 150 rpm, and aliquots were taken at predetermined intervals over a total adsorption period of 12 h. The time-dependent adsorption uptake, q_t , was then determined according to the following equation:

$$q_t = \frac{(C_0 - C_t)}{m} \times V$$

Here, q_t (mg/g) and C_t (mg/L) represent the adsorption capacity and Li^+ concentration at time t , respectively; C_0 is the initial Li^+ concentration, and V (L) and m (g) are the solution volume and adsorbent mass, respectively. In this formulation, C_0 denotes the initial Li^+ concentration, whereas C_t (mg/L) is the Li^+ concentration at time t . The corresponding adsorption uptake at time t , q_t (mg/g), is calculated using the solution volume V (L) and the adsorbent mass m (g).

1.3.4. Thermodynamics of Li^+ Adsorption

The key thermodynamic parameters were derived according to the equations given below:

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m}$$

$$\Delta G = -RT \ln K_d$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

In these equations, the distribution coefficient K_d (mL/g) is defined from the initial and equilibrium concentrations, C_o and C_e together with the solution volume V (L) and adsorbent mass m (g). The Gibbs free energy change ΔG (kJ/mol) is related to the universal gas constant R (J/mol/K) and the absolute temperature T (K). In addition, ΔH (kJ/mol) and ΔS (J/mol/K) correspond to the enthalpy and entropy changes, respectively.

1.3.5 Reusability Evaluation

Reusability was assessed through six consecutive adsorption–desorption cycles carried out in a thermostatic shaker. In each cycle, PVV@VLJ-LIS was contacted with 100 mL of Li^+ solution (100 mg/L) and agitated at 150 rpm and 25 °C for 12 h to complete adsorption. The recovered adsorbent was then washed thoroughly with distilled water, followed by desorption in 100 mL of 0.2 M hydrochloric acid. After acid elution, the material was rinsed again with distilled water and reused in the next adsorption run. The residual Li^+ concentration in the aqueous phase was quantified by flame atomic absorption spectrometry (FAAS), and the reusability (R) was calculated according to the equation below:

$$R = \frac{Q_n}{Q_0} \times 100\%$$

In this definition, n refers to the adsorption–desorption cycle number. Q_0 and Q_n (mg/g) denote the Li^+ adsorption capacities of PVV@VLJ-LIS before regeneration and after the n th regeneration cycle, respectively.

1.4 Antibacterial performance tests

Escherichia coli and *Staphylococcus aureus* were selected as representative

bacterial strains. First, the strains were streaked onto LB agar plates using a sterile inoculating loop and incubated at 37 °C for 18 h for activation. A single typical colony was then inoculated into fresh nutrient broth and cultured to the logarithmic phase, and the bacterial suspension was adjusted to approximately 1×10^8 CFU/mL according to the 0.5 McFarland standard. The suspension was further diluted to 1×10^6 CFU/mL for subsequent antibacterial tests. A sample (3 cm in diameter) was brought into full contact with 1 mL of bacterial suspension (1×10^6 CFU/mL) and incubated for 6 h under light and dark conditions, respectively. After incubation, the bacterial suspension was collected and serially diluted. Aliquots (100 μ L) of appropriately diluted suspensions were spread uniformly onto plate count agar and incubated at 37 °C for 24 h. The number of viable bacteria was then calculated based on the colony counts.

2. Density functional theory calculations

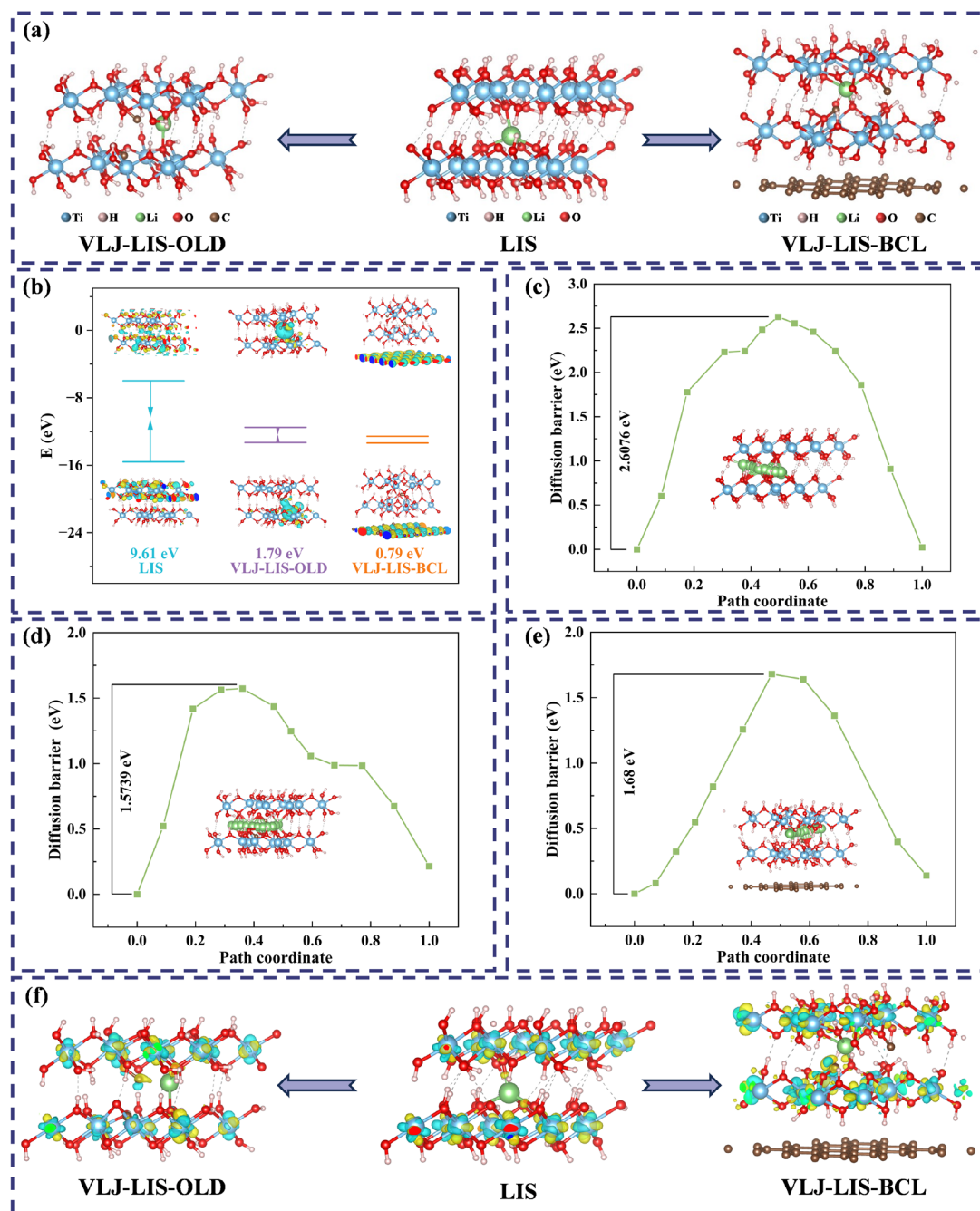


Fig. S1. (a) Structural models of the LIS, organic-component local doping structural model of VLJ-LIS (VLJ-LIS-OLD) and biomass carbon-coated structural model of VLJ-LIS (VLJ-LIS-BCL). (b) HOMO - LUMO energy gaps. (c) Li⁺ diffusion energy barrier of the LIS model. (d) Li⁺ diffusion energy barrier of the VLJ-LIS-OLD model. (e) Li⁺ diffusion energy barrier of the VLJ-

LIS-BCL model. (f) Differential charge density maps of the LIS, VLJ-LIS-OLD and VLJ-LIS-BCL model.

To elucidate the effect of VLJ-modified lithium-ion sieves on adsorption behavior from a mechanistic perspective, density functional theory calculations were used to further investigate the changes in adsorption performance after modification. As shown in Fig. S1a, the structural model of LIS consists of a typical Ti–O inorganic framework together with surface hydroxyl groups and oxygen-containing coordination environments, exhibiting an overall layered stacking feature. The adsorbed ions are located near surface adsorption sites and form localized interactions with surrounding oxygen-containing sites. Considering that Vaccinium leaf juice (VLJ) may participate in surface structural modification in different forms during high-temperature treatment under an inert atmosphere, two modified lithium-ion sieve models were constructed in this work. To investigate the local regulation effect of carbonized components introduced by VLJ after high-temperature treatment under an N₂ atmosphere on adsorption sites, the organic-component local doping structural model of VLJ-LIS (VLJ-LIS-OLD) was established. To further investigate the structural characteristics of a continuous biomass carbon-coated layer formed on the LIS surface after VLJ modification, the biomass carbon-coated structural model of VLJ-LIS (VLJ-LIS-BCL) was constructed.

To supplement the information on the energy levels and spatial distributions of local frontier electronic states near the interface, the three-dimensional isosurfaces and corresponding energy levels of the HOMO and LUMO for different structural models

were further investigated. As shown in Fig. S1b, the energy gaps of the three structural models decrease in the following order: LIS (9.61 eV), VLJ-LIS-OLD (1.79 eV), and VLJ-LIS-BCL (0.79 eV). Compared with the unmodified structural model, the introduction of VLJ leads to a pronounced narrowing of the frontier energy-level gap, while the spatial distribution of the frontier orbitals shifts from being dominated by the inorganic framework to the joint participation of organic components, biomass carbon components, and interfacial regions. The narrowed energy gap, together with the continuous distribution of frontier orbitals in interfacial and carbon-related regions, indicates that more frontier electronic states capable of participating in electronic responses are available near the interface, facilitating charge rearrangement and providing more favorable electronic structural conditions for the rapid establishment of interactions between Li^+ and surface adsorption sites.

The migration process of Li^+ between adjacent stable adsorption sites in the three structural models was investigated using the nudged elastic band (NEB) method, and the corresponding configurational evolution along the migration pathway and the variation in energy as a function of the reaction coordinate are shown in Fig. S1c–e. For the LIS model, the energy profile rises sharply in the middle of the migration pathway and forms a single pronounced peak, yielding a migration barrier of 2.6106 eV, indicating that Li^+ must overcome a high barrier to hop between sites. After the introduction of organic components, the VLJ-LIS-OLD model exhibits an overall downward shift in the energy profile with a significantly reduced peak, resulting in a migration energy barrier of 1.5739 eV. In addition, a relatively flat energy region

appears after the peak, indicating that the energetic cost of the rate-limiting step during migration is substantially reduced. The migration energy barrier of VLJ-LIS-BCL is 1.68 eV, which is markedly lower than that of LIS but slightly higher than that of VLJ-LIS-OLD. These results demonstrate that both modified structural models can effectively reduce the migration energy barrier of Li^+ , implying that site-to-site hopping of Li^+ is more likely to occur under identical thermal activation conditions, which is theoretically favorable for ion diffusion and replenishment during the adsorption process.

To elucidate the electronic structural origins underlying the differences in adsorption energies among the structural models, the differential charge density distributions before and after adsorption were analyzed. As shown in Fig. S1f, all three structural models exhibit charge redistribution in the oxygen-containing coordination regions adjacent to Li^+ , reflecting charge polarization and electrostatic interactions between Li^+ and surface O sites. Notably, the VLJ-LIS-BCL structural model displays stronger and more continuous charge rearrangement near the interface between the inorganic framework and the carbonaceous layer, indicating enhanced interfacial polarization and a more pronounced local electric field, which more effectively stabilizes the adsorbed Li^+ .

3 Stability performance

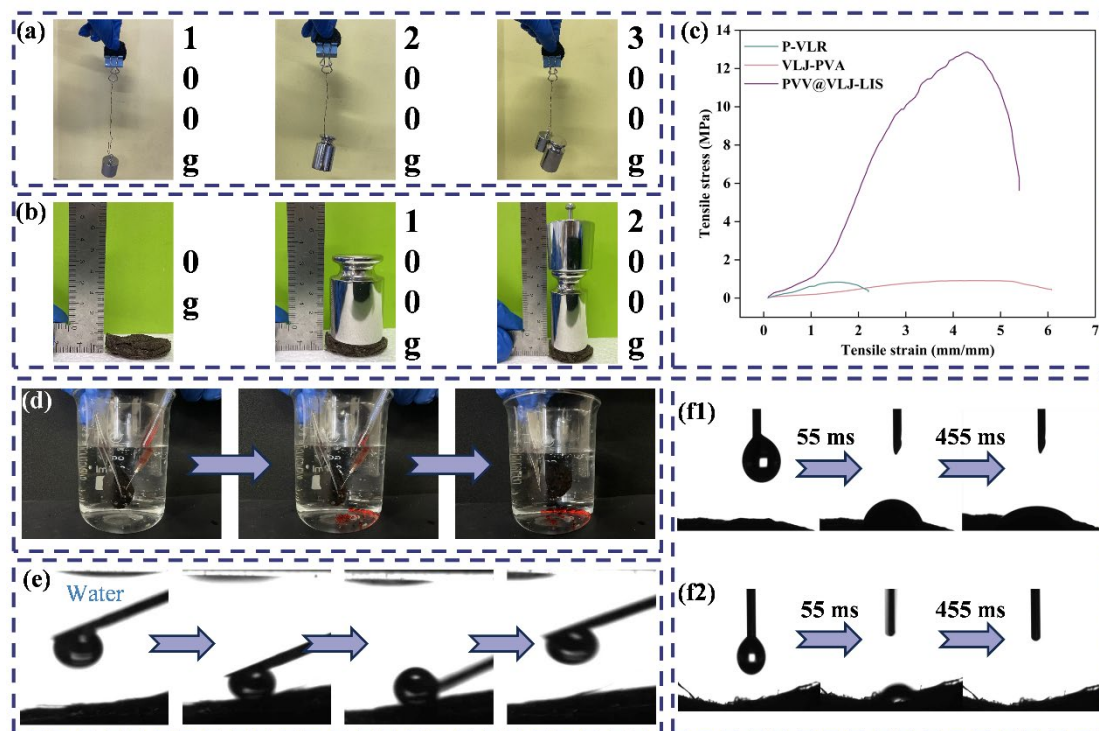


Fig. S2. (a) Tensile properties of PVV@VLJ-LIS. (b) Load-bearing test of PVV@VLJ-LIS. (c)

Stress–strain curves of PVV@VLJ-LIS. (d) Anti-fouling property tests using PVV@VLJ-LIS. (e)

The images showing underwater anti-oil fouling properties of PVV@VLJ-LIS. (f) The water

contact angle (WCA) of VLJ-PVA and PVV@VLJ-LIS.

To evaluate the structural stability and overall mechanical strength of PVV@VLJ-LIS, tensile and compressive tests were conducted, with the results shown in Fig. S2a and Fig. S2b, respectively. The tensile results indicate that PVV@VLJ-LIS remained intact without fracture when the external load was increased to 300 g. The compression test further shows that the sample maintained its integrity as the vertical load was gradually increased to 200 g, with no obvious collapse or structural instability, demonstrating favorable compressive load-bearing capability. The stress–strain curves (Fig. S2c) further reveal differences in mechanical performance among the samples:

compared with P-VLR and the VLJ-PVA hydrogel, PVV@VLJ-LIS exhibits a markedly higher maximum stress, reaching 12.38 MPa, together with an increased elongation at break of 5.821 mm mm⁻¹. These results indicate that the three-dimensional crosslinked network formed via the freezing and salting out process can effectively enhance the mechanical properties of the material.

To further evaluate the antifouling performance of PVV@VLJ-LIS, underwater oil-droplet contact and anti-oil adhesion tests were performed. As shown in Fig. S2d, oil droplets slid off the evaporator surface rapidly under water with almost no residue, indicating strong underwater anti-oil fouling for PVV@VLJ-LIS. The underwater anti-oil adhesion results (Fig. S2e) show that oil droplets remained nearly spherical upon contact with the PVV@VLJ-LIS surface and detached rapidly upon slight disturbance, demonstrating underwater oleophobicity. This observation is attributable to the abundance of hydrophilic functional groups on the PVV@VLJ-LIS surface, which readily bind water molecules to form a stable hydration layer, thereby reducing the propensity of oil contaminants to adhere to the surface. The hydrophilicity test (Fig. S2f1) shows that a water droplet spread rapidly on PVV@VLJ-LIS within 55 ms and reached complete wetting at 455 ms, indicating superhydrophilicity. By contrast, VLJ-PVA still retained a partially cap-shaped droplet at 455 ms (Fig. S2f2), indicating that the three-dimensional porous network jointly constructed by the leaf residue and VLJ-PVA promotes water transport. Overall, the superhydrophilicity and underwater oleophobicity of PVV@VLJ-LIS underpin its antifouling capability and efficient evaporation in complex seawater environments.



Fig. S3. (a) Electrical resistance of seawater, purified water and tap water. (b) Digital photographs of methyl orange (MO) and methylene blue (MB) solutions before and after purification. (c) pH values of acetic acid and NaOH solutions before and after purification. (d) Digital photographs of PVV@VLJ-LIS after immersion in solutions with different pH values for 72 h.

The ionic content of seawater, purified water and tap water was evaluated by measuring their electrical resistance. As shown in Fig. S3a, the resistance of seawater was 73.8 kΩ, whereas the resistances of purified water and tap water were 1.08 MΩ

and 0.63 M Ω , respectively. This difference arises from the markedly reduced concentration of metal ions in the purified water, which leads to a higher resistance. The higher resistance of purified water compared with tap water further indicates a lower ionic content in the purified water. In addition, to verify the capability of the evaporation-adsorption material PVV@VLJ-LIS to purify dye wastewater, methylene blue (MB, 100 mg/L) and methyl orange (MO, 100 mg/L) solutions were prepared, evaporated under a xenon lamp, and the collected condensate was analysed. As shown in Fig. S3b, the treated solutions became nearly transparent after purification. These results indicate that the evaporated water contains negligible amounts of the two organic dyes, demonstrating that PVV@VLJ-LIS is effective for purifying wastewater containing methylene blue and methyl orange. This feature is also beneficial for the coupled operation of evaporation and lithium adsorption under complex seawater conditions.

In addition, to further verify the evaporation performance of PVV@VLJ-LIS under harsh conditions, evaporation tests were conducted using simulated acidic and alkaline solutions. As shown in Fig. S3c, photothermal evaporation was performed using an acidic solution (0.1 M acetic acid) and an alkaline solution (1 M NaOH), and the pH of the collected water was close to neutral. Therefore, the evaporation-adsorption material PVV@VLJ-LIS exhibits a purification effect for both acidic and alkaline solutions, indicating its applicability in a range of scenarios. Digital photographs of PVV@VLJ-LIS after immersion in solutions of different pH values for 72 h are shown in Fig. S3d. After immersion over the pH range of 2–12, PVV@VLJ-

LIS maintained an intact overall morphology without obvious fragmentation or disintegration, demonstrating excellent acid-alkali tolerance.

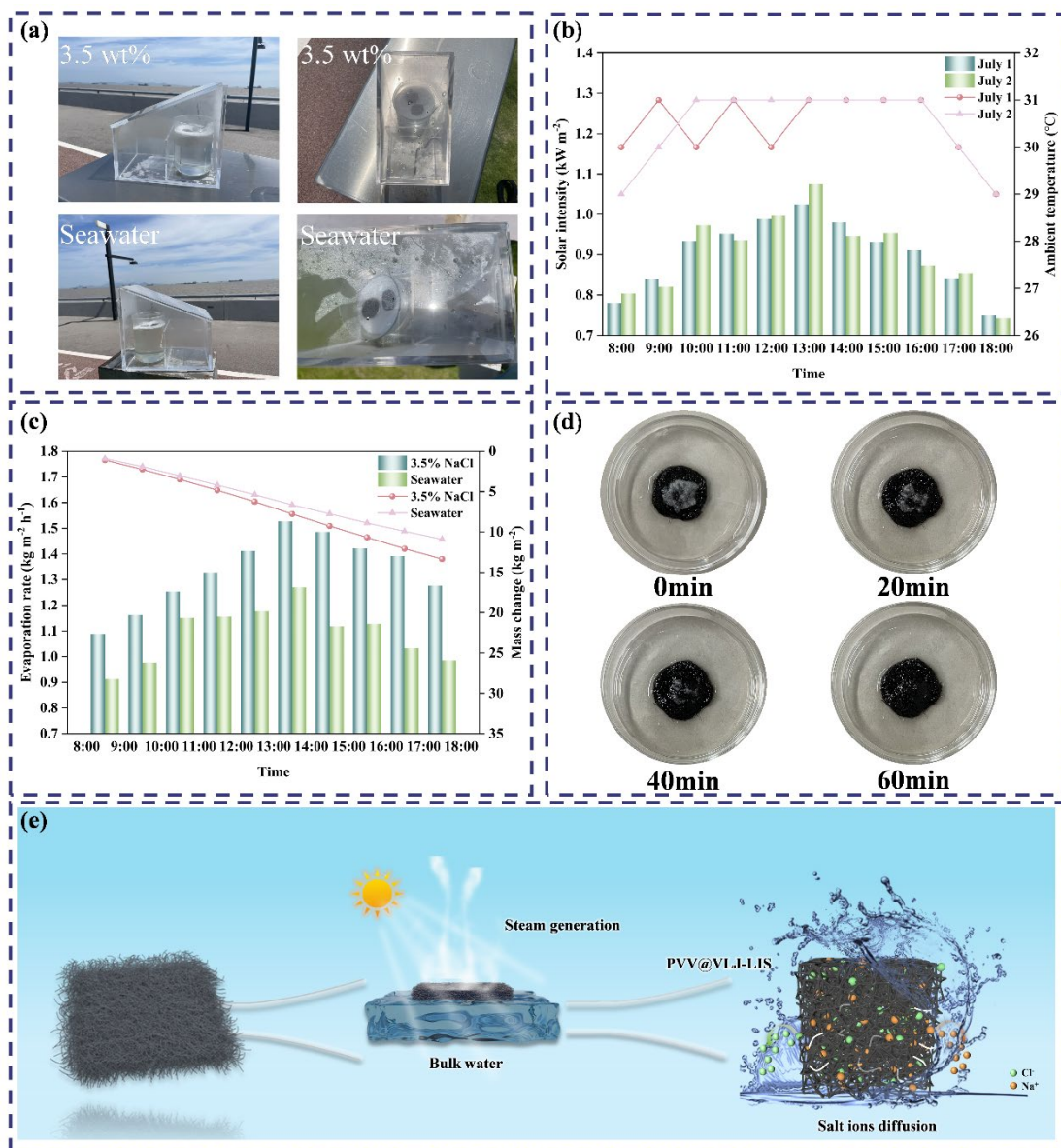


Fig. S4. (a) Schematic of the evaporator device. (b) Temporal evolution of solar flux and ambient temperature (08:00–18:00) on July 1–2, 2025. (c) Time-dependent evolution of the evaporation rate and mass change of the outdoor evaporator system in natural seawater and 3.5 wt % NaCl solution from 08:00 to 18:00. (d) The diffusion of NaCl on the surface of PVV@VLJ-LIS. (e)

Schematic illustration of the self-desalting mechanism of PVV@VLJ-LIS.

To assess the evaporation performance and durability of PVV@VLJ-LIS under realistic outdoor conditions, field tests were carried out. The feedwaters included natural seawater from the East China Sea and a synthetic 3.5 wt % NaCl solution prepared in the laboratory. Condensate was collected using the apparatus shown in Fig. S4a, and outdoor tests were carried out on 1–2 July 2025. The temporal variations in solar irradiance and ambient temperature are shown in Fig. S4b: the average ambient temperatures were 30.5 °C and 30.0 °C over the two days, and the solar irradiance ranged from 0.742 to 1.075 kW m⁻². As shown in Fig. S4c, PVV@VLJ-LIS achieved a maximum evaporation rate of 1.528 kg/(m²·h) in natural seawater, which is comparable to that measured under laboratory conditions. In addition, no obvious salt deposition was observed on the PVV@VLJ-LIS surface after continuous evaporation for 10 h, indicating effective self-desalting performance that supports sustained evaporation in complex natural environments. To further evaluate the salt-rejection capability of PVV@VLJ-LIS, 0.3 g of NaCl was evenly placed on its surface and tested under natural light (Fig. S4d). The salt crystals completely dissolved within 60 min, further demonstrating strong resistance to salt accumulation.

As illustrated in Fig. S4e, the self-desalting capability of PVV@VLJ-LIS mainly arises from its three-dimensionally interconnected porous channels and hydrophilic network architecture. First, the hydrophilic network enables continuous water supply from the bulk solution to the evaporation interface, thereby alleviating salt accumulation at the interface. Second, the interconnected channels provide transport pathways for salt ions to diffuse from the evaporation interface back into the bulk

solution under a concentration gradient. Under illumination, continuous evaporation at the interface generates water vapour, while salt ions diffuse into the bulk solution driven by the concentration gradient. This coupled process suppresses salt crystallisation on the PVV@VLJ-LIS surface and sustains a high evaporation rate.

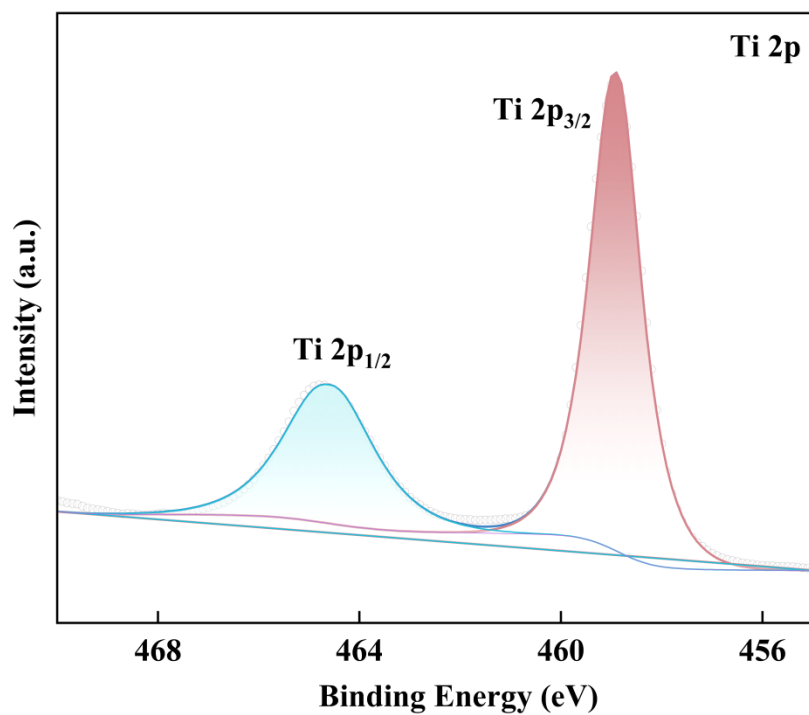


Fig. S5. Ti 2p XPS spectrum of VLJ-LIS.

Tab. S1. Fitted kinetic parameters for Li⁺ adsorption on LIS and VLJ-LIS

	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (h ⁻¹)	q_e (mg/g)	R ²	k_2 (g/mg/h)	q_e (mg/g)	R ²
LIS	0.4436	26.38	0.97819	0.01853	32.96	0.99651
VLJ-LIS	0.7198	20.72	0.95414	0.0471	29.57	0.99522

Tab. S2. Fitted kinetic parameters for Li⁺ adsorption on PVV@VLJ-LIS

PVV@VLJ-LIS	Pseudo-first-order model			Pseudo-second-order model		
Temperature	k_1 (h ⁻¹)	q_e (mg/g)	R ²	k_2 (g/mg/h)	q_e (mg/g)	R ²
25 °C	0.52	12.94	0.9869	0.0883	14.47	0.99987
30 °C	0.48	15.01	0.9789	0.0758	15.17	0.99989
35 °C	0.46	16.41	0.97958	0.0722	16.58	0.99989
40 °C	0.44	17.47	0.98011	0.0718	17.68	0.99988

Tab. S3. Thermodynamic fitting parameters for Li⁺ adsorption on PVV@VLJ-LIS

Sorbent	ΔH° (kJ/mol)	ΔS° (J/mol/K)	T (K)	K°	ΔG° (kJ/mol)	R ²
PVV@VLJ-LIS	16.51	72.14	298.15	7.37	-4.96	0.97855
			303.15	8.56	-5.41	
			308.15	9.44	-5.74	
			313.15	10.16	-6.04	