A hydrogel-based antifouling solar evaporator for highly efficient water desalination

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Solar desalination is a promising method for large-scale water purification by utilizing sustainable energy. However, current high-rate solar evaporation often relies on optical concentration due to the diffusion of natural sunlight which leads to inadequate energy supply. Here we demonstrate a hydrogel-based solar evaporator capable of generating vapor at a high rate of ~2.5 kg m$^{-2}$ h$^{-1}$ under one sun irradiation (1 kW m$^{-2}$), among the best values reported in the literature. Such highly efficient solar evaporation is achieved by a hybrid hydrogel composed of hydrophilic polymer framework (polyvinyl alcohol, PVA) and solar absorber (reduced graphene oxide, rGO), which has internal capillary channels. The PVA can greatly facilitate the water evaporation owing to reduced water evaporation enthalpy in hydrogel network. The rGO penetrating in the polymeric network enables efficient energy utilization. The capillary channels sustain an adequate water supply for continuous solar vapor generation at a high rate. Such hydrogel-based solar evaporator also exhibits the promising antifouling property, enabling long-time water desalination without recycling. The high-efficiency hydrogel-based solar vapor generators open significant opportunities to enhance solar water evaporation performance and reduce the cost of solar desalination systems.

Introduction

Freshwater scarcity is one of the most serious threats to the development of human civilization.\textsuperscript{1, 2} Among various strategies to alleviate the issue of freshwater shortage, seawater desalination offers an adequate production of high-quality water without impairing natural freshwater ecosystems.\textsuperscript{3} Compared with traditional seawater purification technologies, such as reverse osmosis and ion exchange, some novel distillation systems have demonstrated the promising potential of evaporation-based water purification due to high efficiency, low cost and scalability.\textsuperscript{4} In this context, exploring sustainable solar energy to power the water evaporation becomes a rapidly growing research direction.\textsuperscript{5} Tremendous attention has been paid to increase the efficiency of solar desalination, where the key design principles can be generally summarized as follows: (I) enhancing the solar absorption to harvest energy from concentrated sunlight; (II) confining the converted energy to the small amount of water at the evaporation surface.\textsuperscript{6-8} For instance, various absorbers with broadband and enhanced light absorption, such as ultra-black semiconductors,\textsuperscript{9} and
Hydrogels, a unique class of polymer materials with 3D cross-linking structures, have been investigated for vapor generation under concentrated solar irradiation. However, despite the high evaporation rate, large-scale application of such materials or designs is hindered by the relatively low energy efficiency and the high cost of complex optical concentrators. In addition to light concentration, improving energy confinement by heat localization and converted by the absorber can be directly delivered to the evaporation surface assisted with both capillary pumping and osmotic swelling effects, alleviating the water loss during evaporation. rGO absorbers, interpenetrating within the polymeric network (PVA), can efficiently harvest solar energy as well as transfer and confine energy to the molecular meshes on the evaporation surface, where the water evaporation is facilitated, further accelerating the water evaporation.

Upon exposure to the solar radiation, strong water evaporation (blue arrows) can be powered by solar energy. The floating CTH is capable of transporting the water from bulk water to the evaporation surface assisted with both capillary pumping (pink arrows) and osmotic swelling (light blue arrows) effects, alleviating the water loss during evaporation. rGO absorbers, interpenetrating within the polymeric network (PVA), can efficiently harvest solar energy as well as transfer and confine energy to the molecular meshes on the evaporation surface, where the water evaporation is facilitated, further accelerating the water evaporation.
the potential application of such low-cost and scalable CTHs is demonstrated by a continuous solar desalination for 96h showing a very high yet stable efficiency.

Results and discussion

Fig. 2 Chemical and Structural Characterization of the CTH. (a) Photograph of a large piece (20 X 30 cm) of as-prepared CTH; (b-d) SEM images in different magnification showing (b) cross-section image of capillary channels from top-view (c) micron-sized pores and (d) distorted surface of the wall structure of the CTH. Inset of (d): flat surface of the wall structure in pure PVA hydrogel, scale bar is 100 nm. (e) Dynamic mechanical analysis showing storage modulus (G’) and loss modulus (G″) of PVA and CTH. (f) FTIR spectra of PVA, rGO and the CTH showing the chemical composition.

were investigated by the scanning electron microscopy (SEM). Fig. 2f were shown in Fig. 2f. The spectrum of PVA (blue curve) shows the 2b shows the cross-section of the capillary channels inside the CTH as absorption signal at 1110 cm⁻¹, which can be attributed to the C-O with a diameter of about tens of microns, which is profiled by red stretching and is a characteristic peak of PVA. In the spectrum of dashes. In addition, the small pores distributing on the wall up to CTH hydrogel, scale bar is 100 nm. All the characteristic peaks of several microns (Fig. 2c). Fig. 2d shows the roughened surface of PVA and rGO can be found in the spectrum of the CTH (black curve), the wall with rGO in the network of PVA, compared with the flat confirming the presence of rGO in the PVA polymeric network. And smooth surface of pure PVA hydrogel (Inset of Fig. 2d). Considering the results of thermogravimetric analysis (TGA) as shown in Fig. S2 a swelling ratio (ca. 270 %) of the fully hydrated wall structure (Fig. S1, ESI†), the width of the capillary channels in fully hydrated CTHs. To systematically assess the influence of rGO additive on the transport of the CTH.

Owing to its viscoelasticity, the hydrogels present both energy and dissipation under oscillatory stress. All the characteristic peaks of pVA, CTH1, CTH2, CTH3 and CTH4 were shown in Fig. 2f. The spectrum of PVA (blue curve) shows the important features of C-H stretching and is a characteristic peak of PVA. The C=C stretching in the aromatic rings. All the characteristic peaks of several microns (Fig. 2c). Fig. 2d shows the roughened surface of PVA and rGO can be found in the spectrum of the CTH (black curve), the wall with rGO in the network of PVA, compared with the flat confirming the presence of rGO in the PVA polymeric network. And smooth surface of pure PVA hydrogel (Inset of Fig. 2d). Considering the results of thermogravimetric analysis (TGA) as shown in Fig. S2 a swelling ratio (ca. 270 %) of the fully hydrated wall structure (Fig. S1, ESI†), the width of the capillary channels in fully hydrated CTHs.

components of the polymeric network in the CTHs. Fig. 2e shows where W is the weight of the water in the swollen G' and G" values of the CTH and a pure PVA gel. The dynamic sample and the corresponding dried aerogel sample, respectively. Frequency sweep experiments of both gels show a wide linear range of the swelling capacity of the CTH can be evaluated by the saturated viscoelastic region. The higher storage modulus compared with a pure PVA hydrogel, i.e. g g⁻¹, respectively, indicating that the Q, of the CTHs pure PVA hydrogel, indicating extra physical cross-linking points can be tuned by the oxygen-containing level of rGO additives. In relative to PVA hydrogel due to the interaction between RGO and CTH, the water transport in CTHs is evaluated by the dynamic PVA chains. These results demonstrate that the rGOS are analysis of their swelling process. Given that the CTHs are nearly penetrated in the polymeric network of PVA hydrogels. Such hydrogels are completely hydrated during solar vapor generation, the swollen structure is significant for efficient energy utilization (vide infra). Time from the half-saturated state (i.e. 0.5 Q) to the saturated state in order to analyze the chemical composition of the CTH, the (i.e. Q) can reveal the water transport in the CTHs (Fig. 3b). As Fourier-Transform infrared (FTIR) spectra of PVA, rGO, and the CTH showing in Fig. S4 (ESI†), all the Q values of CTH1 to CTH4 present...
To investigate the solar absorption ability, UV-vis-NIR \( \lambda \) continuously escaped from the surface of the CTH to the air under spectrophotometer was used to measure the light absorption of \( \lambda \) constant solar illumination, the overall mass change with and CTHs. As shown in Fig. 3c, the CTHs present excellent full solar \( \lambda \) without the CTHs was recorded once the temperature reached spectrum light absorption with a negligible optical loss. In addition, \( \lambda \) steady state (pre-heating for ca. 30 min), representing the amount the CTHs showed low reflectance in the wavelength range from 250 \( \lambda \) to 2500 nm (Fig. 5a, ESI†). These results indicate that the light \( \lambda \) is much faster than that of pure water under one sun radiation. In absorption of the CTHs does not depend on the Q and V values, \( \lambda \) addition, based on optimized PVA/water (Fig. 5 and 6, ESI†) and ensuring stable solar energy harvesting for vapor generation. In \( \lambda \) both rGO/PVA (Fig. S9 and S10, ESI†) ratio, the CTH3 presents the highest order to quantitatively analyse the light absorption, the \( \lambda \) water evaporation rate of \( \sim 2.5 \) kg m\(^{-2}\) h\(^{-1}\) (Fig. S11, ESI†), among all transmittance of CTHs with different thicknesses were carefully \( \lambda \) CTH 1-4 samples (Fig. 4a and Fig. S12, ESI†). Compared with CTH3, measured by the UV-vis-NIR spectrophotometer. A CTH sheet with \( \lambda \) CTH1 and CTH2 samples showed inefficient water transport which a thickness of ca. 400 \( \mu \)m provides average transparency of ca. 2% \( \lambda \) seriously limits the evaporation rate. Despite the fast water (Fig. 5b, ESI†), indicating efficient solar energy harvesting of CTH. \( \lambda \) transport in CTH4, the excessive water content would reduce the To investigate the photothermal behaviour of the CTH under one \( \lambda \) energy utilization efficiency as more energy will be used to heat the sun, the temperature variations of CTH surface and bulk water were \( \gamma \) water. Note that all the experimental data of solar vapor carefully traced (Fig. 3d). The free-floating CTHs show a rapid \( \lambda \) generation were calibrated with dark evaporation data (see surficial temperature increase within 5 min, while the temperature \( \gamma \) Experimental Section for details). The corresponding energy of bulk water remains nearly constant. The CTHs 1-4 present similar \( \lambda \) efficiency \( (\eta) \) is calculated by the following formula \( \eta = \frac{\dot{m} h_v}{C_{opt} P_0} \) (3)

bulk water is found to be maintained \( \sim 25^\circ\)C in 1 h, evidencing the \( \omega \) in which \( \dot{m} \) is the mass flux, \( h_v \) is the vaporization enthalpy of the effective energy confinement in the CTHs. \( \omega \) water in CTHs, \( P_0 \) is the solar irradiation power of one sun (1 kW

To measure the efficiency of solar vapor generation, the CTHs \( \sim 2^3 \), and \( C_{opt} \) refers to the optical concentration on the absorber free-floating on the bulk water were exposed to solar radiation (1 \( \alpha \) surface. It should be noted that the vaporization enthalpy of water \( \sim 2^4 \) kW m\(^{-2}\)) for a typical vapor generation test (Fig. 1). As the water \( \alpha \) can be reduced by the polymeric network of hydrogels.\( \alpha \) The

linear dependence over time during the swelling. The water transport rate (V) can be calculated by

\[ V = \frac{0.5Q_0}{t} \] (2)

where \( t \) is the half-swollen time (blue points in Fig. 3b). Upon one gram of xerogel, the CTH1, CTH2, CTH3 and CTH4 show the V of \( \alpha \).

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Fig. 3. Tunable water transport, solar absorption and solar thermal conversion of the CTHs. (a) The saturated water content in CTHs per gram of corresponding xerogel (i.e. g g\(^{-1}\)). The CTH1 to CTH4 represent gels containing rGO with the C/O ratio of 132.3, 19.6, 12.7 and 4.9, respectively. (b) The swollen behavior of CTHs from half-saturated to saturated state and calculated water transport rate indicate the tunable water transport in CTHs. (c) UV-vis-NIR spectra of CTH sheets with a thickness of ca. 1 mm. The normalized spectral solar irradiance density of air mass 1.5 global (AM 1.5 G) solar spectrum is shown by the black dashed line. (d) The temperature of evaporation surface in CTHs and bulk water under one sun irradiation over time. W-CTH1,2,3 and 4 represent the temperature of bulk water underneath CTH 1,2,3 and 4, respectively.
vaporization enthalpy used here is smaller than the classic latent enthalpy of water (Fig. S13 and S14, ESI†). The CTH realized a high energy efficiency of up to ~95% under one sun (Fig. S15, ESI†). Since the water evaporating rate upon one sun directly reflects the promise of solar vapour generation under ambient conditions and natural sunlight, the high rate achieved by CTH3 (red sphere in Fig. 4b)15, 16-18, 20-22, 26, 27 indicates a potential application of CTHs in practical solar vapor generation.

Fig. 4 Solar vapor generation of the CTH under one sun. (a) The mass loss of water for different CTH samples under one sun (1 kW m$^{-2}$) in comparison of pure water as the control test. (b) One-sun vapor generation performance of CTH3 compared with recent literature reports. (c) The setup for solar vapor generation test based on the CTH and corresponding infrared images showing the temperature distribution with irradiation time of 0 min, 10 min, and 60 min. (d-e) Modelling and theoretical simulation of temperature distribution near the evaporation surface of CTH, where the red olivary areas and blue background represent the capillary channels and polymeric network, respectively. The preloaded heat and water source are depicted by yellow and blue dashed arrows, respectively.

To investigate the energy utilization of CTH, infrared imaging was used to monitor the temperature rise in the solar evaporation at 305 K (~32 °C) at the surface of polymeric network (Fig. 4e). This result is close to our experimental results, confirming the effective comparison of the photograph and infrared images of the solar heat confinement based on the CTHs. Additionally, the biphasic evaporation system with exposure time of 0 min, 10 min and 60 min mixture model was used to simulate the water transport in the min clearly show that the CTH is heated to ~32 °C and the CTHs to further confirm the adequate water supply (see temperature of bulk water is barely changed, indicating that the Supplementary Methods in ESI† for details).18 The 2D mapping of converted energy is confined in the CTH, rather than diffused to the water velocity distribution depicts fast water transport through the bulk water. To further clarify the energy confinement near the internal gaps to recover surficial water loss (Fig. S16, ESI†).

To demonstrate the potential application, the CTH is used as the evaporator in a solar desalination system (Fig. 5a). The floating modeling in which the capillary channels and polymeric network CTH harvests solar energy to vaporize the water (blue arrow). The were simulated by long olivary area (red, with width of 10 μm) and vapor is collected as purified water through condensation, quadrature background (blue) in a 2D mapping, respectively. The achieving the water desalination. Moreover, an equilibrium is established when the water transport induced salt ion absorption respectively. A basic heat-transfer model was employed to describe (violet arrow) and diffusion enabled salt ion discharge (yellow temperature distribution in the CTH3 (see Supplementary Methods arrow) are balanced. To evaluate the effect of solar desalination in ESI† for details).11 The heat and water input were preloaded at based on CTH3, a real seawater sample (from the Gulf of Mexico) the surface (Z = 500) and the bottom (Z = 0), respectively. After the was used for desalination test, and the quality of collected purified temperature distribution reaches the steady state, the simulation water was measured by the inductively coupled plasma
It is found that the concentration of all the four primary ions (Na\(^+\), Mg\(^{2+}\), K\(^+\) and Ca\(^{2+}\)) were significantly reduced by two orders (Fig. 5b) after solar desalination. In addition, three artificial seawater samples with representative salinities of the Baltic sea (0.8 wt%), world ocean (3.5 wt%) and the Dead Sea (10 wt%) were also used to evaluate the solar desalination, where the salinity of corresponding purified water decreased about four orders of magnitude (Fig. S17, ESI†). These results indicate effective solar desalination based on CTH3.

**Fig. 5 CTH-based solar desalination under one sun.** (a) Schematic illustration of solar desalination based on the CTH. The floating CTH harvests solar energy to vaporize the water for purification (blue arrow). An equilibrium is established when the water transport induced salt ion absorption (violet arrow) and diffusion enabled salt ion discharge (yellow arrow) are balanced. (b) Measured concentrations of four primary ions in an actual seawater sample before and after desalination. (c) Measured concentrations of four primary ions accumulated in CTHs over time, evidencing a relatively low equilibrium ion concentration in used CTH, which was not high enough to trigger the crystallization. (d) The duration test of the CTH based on a continuous solar desalination for 96 h under one sun.

The lifetime of solar evaporators, which is defined by the water distribution can be regulated by the polymeric network reusability, durability and recyclability, is another important aspect and its interaction with rGO additives to balance the water of solar desalination. As shown in Fig. 5c, the concentration of salt transport and solar evaporation, hence improving the residual in the CTHs, is almost constant during a continuous solar desalination efficiency of energy utilization. More importantly, the CTH desalination for 96h, suggesting the restricted ion accumulation, embodies a new possibility to develop high-rate solar and hence indicating the crystalline antifouling functionality (see evaporators under weak sunlight by confining the heat to the Fig. S18, ESI†). Furthermore, the CTH presented a stable molecular meshes, and hence reducing the energy loss. evaporation rate under continuous one sun irradiation over 96 h. Furthermore, the polymeric network can reduce the energy (Fig. 5d) and the CTH retain its evaporation rate and antifouling demand of water vaporization to facilitate the vapor property even the salinity of seawater is 20% (see Fig. S19 and S20. generation. Such a novel design enables a solar vapor ESIF†), showing the excellent durability toward solar irradiation and generation rate of ~ 2.5 kg m\(^{-2}\) h\(^{-1}\) with the energy efficiency of reactive salty ions. Given all above measurements, the CTH ~ 95 % under one sun irradiation. In addition, the antifouling exhibited a promising solar desalination performance for long-term functionality, low cost and scalability further promise the operation in practical environment.

**Conclusions**

In conclusion, highly efficient solar vapor generation has been achieved by our designed hybrid hydrogels with capillarity facilitated water transport (CTH), which offer synergistic features of tailored water transport, effective energy confinement and reduced water vaporization enthalpy. The
Experimental Section

Materials

Chemicals including PVA with average molecular weight of 15 000, hydrochloric acid (37%), graphite powder, graphite flakes (325 mesh), potassium permanganate, sulfuric acid (98%), sodium nitrate, hydrazine monohydrate, glutaraldehyde were purchased from Sigma-Aldrich.

Fabrication of the CTH

In a typical synthesis, PVA (1 g), glutaraldehyde (125 μL, 50%wt in DI water) and DI water (10 mL) were mixed together by sonication (Solution A). Then graphene oxide (100 μL, 3% wt) and HCl (50 μL, 1.2 M) solutions were added to 1 mL of solution A, the gelation was carried out for 2 h. The obtained gel was immersed into DI water overnight to obtain pure hybrid hydrogel. The purified gel was frozen by liquid nitrogen and then thawed in DI water at a temperature of 30 °C. The freezing-thawing process was repeated 10 times. After freeze-drying, the sample was swollen with water and reduced by hydrazine with a temperature of 80 °C overnight. Finally, the CTH was washed with DI water three times to remove extra hydrazine.

Characterization

The morphology and microstructure of samples were observed by Scanning Electron Microscopy (Hitachi, S5500) operating at 5 kV. Before observation, the CTHs were freeze-dried for 24 h. The FTIR spectra of CTHs were recorded by the FTIR Spectrometer (Thermo Mattson, Infinity Gold FTIR) equipped with a liquid nitrogen cooled narrow band mercury cadmium telluride (MCT) detector, using an attenuated total reflection cell equipped with a Ge crystal. To understand the mechanical properties of the CTH, rheological experiments were performed by a rheometer (AR 2000EX, TA instrument) using parallel plate on a peltier plate in a frequency sweep mode. Absorption spectra, transparency and reflectance were recorded using a UV-VIS-NIR spectrometer (Cary 5000) with an integrating sphere unit and automation of reflectance measurement unit. The measurements were corrected by baseline/blank correction with dark correction. Note that we used hydrogel for all the relevant tests and characterization except SEM, baseline/blank correction with dark correction. Note that we used an integrating sphere unit and automation of reflectance measurement unit.

Solar vapor generation measurement

The water evaporation experiments were conducted in the lab with temperature of ca 25 °C and humidity of ca 45% using a solar simulator (AbetTech, M-LS Rev B) outputting simulated solar flux at 1 kW/m² (1 sun). The solar flux was measured by a thermopile (Newport, 818SL) connected to a power meter (Newport, 1916-R). Because the solar flux varies across the beam spot, and the thermopile detector is about 1 cm² in size, the CTH was cut into small pieces with surface area of 1 cm² to have an accurate power input. A CTH chip with thickness of ca. 0.5 cm was floated on pure water (or brine for desalination tests) in a glass cuvette that was set to the beam spot with a solar flux of 1 sun. The mass of the water loss is measured by a lab balance with 0.1 μg resolution and calibrated to weights heavier than the total weight of the setup. The dark condition-evaporation rate was subtracted from the solar-illuminated evaporation rate. All evaporation rates were measured after a stabilization under 1 sun for 30 minutes.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


Efficient solar water evaporation was achieved by antifouling hybrid hydrogels with capillarity facilitated water transport and heat concentration in polymeric network.