Architecting highly hydratable polymer networks to tune the water state for solar water purification

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Water purification by solar distillation is a promising technology to produce fresh water. However, solar vapor generation, is energy intensive, leading to a low water yield under natural sunlight. Therefore, developing new materials that can reduce the energy requirement of water vaporization and speed up solar water purification is highly desirable. Here, we introduce a highly hydratable light-absorbing hydrogel (h-LAH) consisting of polyvinyl alcohol and chitosan as the hydratable skeleton and polypyrrole as the light absorber, which can use less energy (<50% of bulk water) for water evaporation. We demonstrate that enhancing the hydrability of the h-LAH could change the water state and partially activate the water, hence facilitating water evaporation. The h-LAH raises the solar vapor generation to a record rate of ∼3.6 kg m⁻² hour⁻¹ under 1 sun. The h-LAH-based solar still also exhibits long-term durability and antifouling functionality toward complex ionic contaminants.

INTRODUCTION

Rapid, energy-efficient water purification methods are urgently required to address growing water scarcity (1, 2). Solar distillation is a promising technique that uses renewable energy to power the removal of contaminants in water, delivering fresh water to alleviate the freshwater shortage (3, 4). However, solar vapor generation (SVG), the essential process of solar distillation to separate water and contaminants, is energy intensive. Developing materials with an adaptive structure that can efficiently convert solar irradiation to heat and boost water vaporization creates a foundation for solar water purification independent of solar concentrators, opening up opportunities for cost-effective freshwater production. In particular, capillary structures, including porous structure (5–7), directional channel array (8–10), and two-dimensional network (11) as the means to regulate water distribution, have recently been explored using broadband light absorbers such as plasmonic nanoparticles (8, 12–14), carbon materials (5, 6, 15, 16), and semiconductor-based absorbers (17, 18). However, these designs exhibit a limited range of SVG rate (vapor yield, <1.6 kg m⁻² hour⁻¹) under natural sunlight (solar flux, <1 kW m⁻²). Whereas this drawback is caused by the intrinsic energy demand of water vaporization, the hydrated solutes in water have a substantial impact on the phase change behaviors of water by varying the water state (19, 20).

Owing to their tunable physicochemical properties, hydrogel materials consisting of highly hydratable polymer networks and swollen water molecules are conducive to applications in flexible electronics (21, 22), biomedical technology (23, 24), and environmental sensing (25, 26). The hydration of this polymer network opens up possibilities to achieve an intriguing water state distinct from that of bulk water (19, 27, 28). Here, we introduce a light-absorbing hydrogel with highly hydratable polymer networks (termed hydratable light-absorbing hydrogel or h-LAH), made by infiltrating polypyrrole (PPy) absorbers into a matrix consisting of polyvinyl alcohol (PVA) and chitosan. We provide fundamental insights into the links between the involved polymer-water interaction and the resultant variation of water phase change behavior and demonstrate that h-LAH could significantly reduce the energy demand of SVG. Because of the hydration effect, the polymer chains in hydrogels could capture nearby water molecules through strong interaction, such as hydrogen bonding, to form bound water (Fig. 1, deep blue area). In contrast, the water molecules that are separated from the polymer chains [termed as free water (FW)] exhibit identical properties with those in bulk water (Fig. 1, light blue area). There is an intermediate region (Fig. 1, yellow area) between bound water and FW, where the water molecules present relatively delicate interplay with polymer chains and adjacent water molecules. The intermediate water (IW) has been demonstrated as activated water that could be vaporized by less energy compared with bulk water (19, 20, 29, 30). On the basis of this design, the rate of 1-sun SVG could be increased up to 3.6 kg m⁻² hour⁻¹ at an energy efficiency of ~92%. The h-LAH–improved SVG enables highly efficient, scalable, and cost-effective solar water purification of various soluble ionic contaminants with antifouling functionality, as well as long-term durability.

RESULT

Preparation and characterization of h-LAH

The in situ cogelation method is used to construct the polymer network that consists of PVA and chitosan. The PPy was used as an additive endowing the h-LAH with a light-absorbing functionality (see section S1 for details). The as-prepared h-LAHs were black and flexible (Fig. 2A). The configuration of h-LAHs, such as the size and shape, depends on the mold used for gelation, indicating desirable scalability. Scanning electron microscopy (SEM) imaging reveals the cross-section morphology of the freeze-dried h-LAH (Fig. 2B). Pores with a diameter of several microns are uniformly distributed in the h-LAH, which is a typical structural feature, indicating homogeneous gelation throughout the resultant hydrogel. To analyze the chemical composition, we show the Fourier transform infrared (FTIR) spectra of pure PVA, PPy, chitosan, and the h-LAH in Fig. 2C. In the spectrum of PVA (black curve), the peak at 1087 cm⁻¹ represents the C—O stretching, which is a characteristic peak of PVA (31). The spectrum of PPy (red curve) shows the absorption signal at 1451 cm⁻¹, corresponding to the C==C stretching in the pyrrole rings (32). The blue curve represents the spectrum of chitosan in which the characteristic peaks are located at 1626 and 1374 cm⁻¹, corresponding to the amid peak of chitosan (31). All the characteristic peaks of PVA, PPy, and chitosan can be found in the spectrum of the h-LAH (purple curve), confirming the existence of PPy in the PVA and chitosan hybrid polymer network.

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Zhou et al., Sci. Adv. 2019;5:eaaw5484 28 June 2019 1 of 7
As viscoelastic materials, hydrogels show energy storage and energy dissipation characteristics. The corresponding storage modulus ($G'$) and loss modulus ($G''$) can be measured to reveal the structural difference of hydrogels (33). To confirm the cogelation of PVA and chitosan, we prepared a PVA/PPy hydrogel as the blank sample (i.e., control sample without chitosan). The higher $G'$ values compared with $G''$ values confirm the cross-linked polymeric skeleton of these hydrogels (Fig. 2D). The higher $G'$ value of the h-LAH compared with PVA/PPy indicates stronger mechanical strength due to the introduction of chitosan, while the higher $G''$ value reveals the steric hindrance of chitosan.

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Fig. 1. Schematic illustration of SVG based on the h-LAH. The h-LAH is made by infiltrating PPy absorbers into a matrix consisting of PVA and chitosan. As PVA can play the role of surfactant, the PPy chains are dispersed uniformly in the cross-linked PVA and chitosan polymer network. Upon exposure to the solar irradiation, h-LAH can generate water vapor using solar energy. The floating h-LAH consists of the hydratable polymer network based on cross-linked PVA and chitosan, which is inter-penetrated by the light-absorbing PPy. The containing water has three different water types—bound water, IW, and FW. Wherein, the IW can be effectively evaporated with significantly reduced energy demand.

Fig. 2. Chemical and structural characterization of the h-LAH. (A) Photograph of as-prepared h-LAH sample. (B) SEM image of the micron-sized pores in the freeze-dried h-LAH. (C) FTIR spectra of PVA (black curve), PPy (red curve), chitosan (blue curve), and the h-LAH (purple curve). a.u., arbitrary units. (D) Dynamic mechanical analysis showing storage modulus ($G'$) and loss modulus ($G''$) of PVA/PPy hydrogel and the h-LAH. Photo credit: Xingyi Zhou, The University of Texas at Austin.
polymer chains (33). In addition, the comparison of \( G' \) and \( G'' \) values between PVA/chitosan hydrogel and the h-LAH confirms that PPy is interpenetrated in the polymer network composed of PVA and chitosan (fig. S1). These above results demonstrate that the PPy is interpenetrated in the PVA/chitosan hybrid polymer network.

**Tunable water state in the h-LAH**

According to the difference of intermolecular hydrogen bonding, including water/polymer bonding, weakened water/water bonding, and normal water/water bonding (Fig. 3A), the water in the hydrated polymer network has been classified into three types: FW (Fig. 3A, light blue color), IW (Fig. 3A, yellow color), and bound water (Fig. 3A, dark blue color), respectively. We analyze the Raman spectra in the region of the O—H stretching to show the hydrogen bonding distinction of water molecules in the h-LAH (see details in section S2.3.1), revealing the water state in the h-LAH (Fig. 3B). The peaks at 3233 and 3401 cm\(^{-1}\) correspond to FW (Fig. 3B) with four hydrogen bonds (two protons and two lone electron pairs are involved in hydrogen bonding with adjacent water molecules), while the peaks at 3514 and 3630 cm\(^{-1}\) are associated with weakly hydrogen-bonded IW (Fig. 3B) (19). Hence, the stronger IW peaks compared with FW peaks indicate a higher proportion of IW in the h-LAH.

Given that the water in each state shows characteristic phase change behaviors (34), such as freezing and melting, the involved energy transfer could be monitored to further confirm that the h-LAHs induced the differentiation of water state. To quantitatively describe the water content (i.e., hydration level) of h-LAHs, we first define a water fraction \( W_{\text{H}_2\text{O}} \) as

\[
W_{\text{H}_2\text{O}} = \frac{W}{W_s}
\]

where \( W \) and \( W_s \) are the weight of water in the h-LAH and the saturated water content of a fully swollen h-LAH, respectively. We use the differential scanning calorimetry (DSC) to reveal the phase change of water (Fig. 3C). The h-LAH with a low \( W_{\text{H}_2\text{O}} \) of 1% (i.e., almost dried sample) presents a straight line without signals of endothermic process (black curve). It has been demonstrated that bound water, which strongly interacts with hydrophilic polymer chains, is nonfreezeable water, while the IW and FW are freezeable (34). Therefore, the water molecules are captured by the polymer network of the h-LAH, forming bound water, when the \( W_{\text{H}_2\text{O}} \) is 1%. In contrast, there are two peaks located at 0° and ~5°C corresponding to the melting of IW and FW, respectively, that could be observed in the fully hydrated h-LAH (i.e., \( W_{\text{H}_2\text{O}} \) is 100%; green curve). In addition, the measured melting point of FW is shifted to a higher temperature with the increase in \( W_{\text{H}_2\text{O}} \) (red, blue, and green curves), which could be attributed to the postponed heating of samples induced by endothermic melting. In contrast, the steep signal of IW (purple curve) is independent of the water content of the h-LAH, indicating that the generation of IW relies on the hydratable polymer network. It should be mentioned that the melting points of IW and FW are close because of the almost similar melting enthalpy of ices with different crystal structures (35).

To obtain a tailored water state that is capable of providing high-proportioned IW, we constructed polymer networks consisting of PVA and chitosan with a different proportion. Wherein, the h-LAH samples with various PVA/chitosan weight ratios from 1:0 (i.e., no chitosan additive), 1:0.05, 1:0.1, and 1:0.175 to 1:0.25 are noted as h-LAH1 to h-LAH5, respectively. Because of the similar carbon/oxygen ratio (i.e., molar ratio of hydrophobic and hydrophilic groups) of PVA and chitosan (Fig. 4A), the obtained polymer networks in h-LAHs show a similar ability to capture water molecules to form bound water (see details in fig. S2, A and B). The amount of IW highly depends on the hydrlabilty of polymer networks, which presents the ability of polymer networks to swell water and can be indicated by the saturated water content of h-LAHs. The saturated water content \( Q_s \) of h-LAHs is represented by

\[
Q_s = \frac{W}{W_d}
\]

where \( W \) and \( W_d \) are the weights of the water in the fully swollen sample and the corresponding dried aerogel sample, respectively. The \( Q_s \) of h-LAHs rises with the proportion of chitosan (Fig. 4B), indicating an increased hydrlabilty. This phenomenon could be attributed to the presence of highly hydratable –NH\(_3\) groups on chitosan chains (36).

To systematically assess the influence of the hydrlabilty of polymer networks on the water state, we calculated the ratio of IW and FW in fully swollen h-LAHs. According to the DSC data (fig. S2, C and D), the ratios of IW to FW in h-LAH1 to h-LAH5 are 0.758, 0.933, 1.124, 1.284, and 1.339, respectively, indicating that h-LAH with a higher hydrlabilty favors the formation of IW (Fig. 4C). These results are consistent with

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**Fig. 3. Water state in the h-LAH.** (A) Schematic of the water in the hydratable polymer network of the h-LAH, showing water/polymer bonding, weakened water/water bonding, and normal water/water bonding. (B) Raman spectra showing the fitting peaks representing IW and FW in the h-LAH. (C) Differential scanning calorimetry (DSC) curves of the h-LAH with different water fraction (i.e., swollen level, 100% refers to the fully swollen state).
the estimation derived by Raman spectra (fig. S3, A to D). To evaluate the benefits of IW to the SVG, we carefully measured the equivalent water vaporization enthalpy through a comparison of h-LAH1 to h-LAH5 and bulk water regarding the spontaneous evaporation (see details in fig. S3E). The equivalent water vaporization enthalpy ($E_{\text{equ}}$) of water in the h-LAHs can be estimated by assuming that the water vaporization is powered by identical energy input ($U_{in}$), which has

$$E_{\text{equ}} = E_0 m_0 / m_g$$

where $E_0$ and $m_0$ are the vaporization enthalpy and mass change of bulk water, respectively, and $m_g$ is the mass change of these h-LAHs. As shown in Fig. 4D, the obtained equivalent water vaporization enthalpy gradually decreases from h-LAH1 to h-LAH5, suggesting that the IW can reduce the overall energy demand of water evaporation (also see fig. S3F). To systematically investigate this effect, we involved hydrogels that consist of less hydratable polymer networks (see details in fig. S3, G to I).

**DISCUSSION**

**Solar water purification based on the h-LAH**

The SVG performance of h-LAHs upon pure water is represented by the mass change of water under 1-sun solar irradiation over time (Fig. 5A). Note that all the h-LAHs are of optimized light absorption (fig. S4A) and thermal management (Fig. 4, B to F) and the experimental data involved were calibrated with dark evaporation data. It is clear that the SVG rate based on the h-LAH is faster than that of pure water. On the basis of the optimized hydrophilic polymer/water ratio (fig. S5, A and B), PPY absorber concentration (fig. S5, C and D), and cross-linking density (fig. S5, E and F), the h-LAH4 exhibited a high vapor generation rate of ~3.6 kg m$^{-2}$ hour$^{-1}$ with an energy efficiency of ~92% among all samples (fig. S5, G and H). The evaporation rate and energy efficiency gradually increased from h-LAH1 to h-LAH4 due to decreasing equivalent vaporization enthalpy. Despite the low water vaporization enthalpy, the h-LAH5 exhibits high water content, hindering the effective energy utilization and restricting the SVG rate (see detailed discussion in section S2.4.2), which shows the significance of balancing factors regarding water content and state in design of hydratable polymer networks for SVG.

We used a real seawater sample (from the Gulf of Mexico) to show the solar distillation based on the h-LAH and evaluated the quality of collected water using inductively coupled plasma mass spectroscopy (ICP-MS). As shown in Fig. 5B, the concentrations of four primary ions ($Na^+$, $Mg^{2+}$, $K^+$, and $Ca^{2+}$) in seawater are significantly reduced by ~2 to 3 orders after purification and were below the values obtained through membrane- and distillation-based seawater desalination techniques (13). To prove the durability of the h-LAH as an evaporator, we tested the SVG rate under continuous 1-sun irradiation over 96 hours (Fig. 5C). The stable evaporation rate shows that the h-LAH presents a promising performance for practical long-term solar desalination with anti fouling functionality (fig. S6A). In addition, the salinities of three brine samples (NaCl solution) with representative salinities of the Baltic...
Sea [lowest salinity, 0.8 weight % (wt %)], World Sea (average salinity, 3.5 wt %) and Dead Sea (highest salinity, 10 wt %) were all significantly decreased (about four orders of magnitude) after desalination, which are about two orders below drinking water standards defined by the World Health Organization (1 per mil; fig. S6, B to E) (13). These results demonstrate effective solar desalination based on the h-LAH.

Figure 5D shows the steady evaporation rate of the h-LAH under strong acid (1 M H2SO4) and alkali (1 M NaOH) solutions, and the pH value of the purified water is close to 7 (Fig. 5, E and F). Moreover, we also conducted the solar purification of water containing mixed heavy metal ions with four representative ions, including Ni2+, Cu2+, Zn2+, and Pt2+, which are the most common heavy metal ions with relatively high concentrations in industrial waste water, based on the h-LAH. As shown in Fig. 5G, the h-LAH exhibits a stable evaporation rate, and the concentrations of heavy metal ions dropped below 1 mg liter$^{-1}$ after purification (Fig. 5G, inset), which are comparable with those of competitive purification techniques designed for the specific ion (Fig. 5H) (37–39). Along with the unique advantages of h-LAH–based solar water purification compared with other methods in terms of core requirements of practical application, the h-LAH presents a remarkable potential for the practical purification of industrial sewage containing multiple ionic contaminants (fig. S7).
CONCLUSION
In conclusion, we demonstrated the regulation of water state in hydrogels via architected the hydratable polymer network, as a new effective means beyond the previous structural designs to endow materials with stronger ability to accelerate solar water evaporation. The hydrophilic functional groups, such as hydroxyl and amino groups, on the polymer network present strong interaction with water molecules. Hence, the hydrability of the polymer network determines the proportion of IW, thus influencing the overall energy demand of vapor generation. The morphology of the polymer network (i.e., pore size), which depends on the cross-linking density, significantly influences the water diffusion within the hydrogel, since those pores serve as water pathways when the water diffuses to the evaporating surface. Note that the “pores” here are not the microscopic scale pores but the molecular level meshes in the polymer network. It is expected that these fundamental design principles regarding molecular engineering will spur the development of next-generation photothermal materials capable of managing the phase transition of water and associated energy conversions.

We also demonstrated highly efficient solar water purification enabled by the light-absorbing hydrogels with hydratable polymer networks (h-LAH) under 1-sun irradiation. The h-LAH showed an ultra-fast water evaporation rate up to ~3.6 kg m⁻² hour⁻¹ and effective water purification removal of over 99.9% of ionic contaminants. The promising performance of h-LAH shows great potential as an antifouling, long-term stable, and cost-effective vapor generator for solar water purification, and the introduction of IW-facilitated SVG provides a new approach for addressing growing challenges at the energy-water nexus.

Characterizations
The SEM images were implemented by SEM (S5500, Hitachi) to observe the morphology and microstructure of the samples. The h-LAHs were freeze-dried for 24 hours before observation. The FTIR spectra were conducted by the FTIR spectrometer (Infinity Gold FTIR, Thermo Mattson) equipped with a liquid nitrogen cooled narrow-band mercury cadmium telluride detector using an attenuated total reflection cell equipped with a Ge crystal. The mechanical properties of h-LAHs were performed by rheological experiments (AR2000EX, TA Instruments) using a parallel plate on a Peltier plate in the frequency sweep mode. Absorption spectra and reflectance were conducted using a UV-Vis-NIR spectrometer (Cary 5000) with an integrating sphere unit and automation of reflectance measurement unit, and the measurements were corrected by baseline/blank correction with dark correction. The Raman spectra were measured via spectrometer (WITec alpha300). The excitation radiation for the Raman emission was produced using a Yttrium aluminium garnet laser that had a single-mode operation at 532 nm. The evaporation and melting behavior of h-LAHs were observed by a differential scanning calorimeter (METTTLER TOLEDO DSC 3). The temperature and melting enthalpy were calibrated by indium. The concentration of ions was tracked by ICP-MS (Agilent 7500ce) with dilutions in 2% HNO₃ to make the loaded ion concentration lower than 10 parts per million.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/6/eaaw5484/DC1

MATERIALS AND METHODS
Chemicals and materials
Chemicals including PVA with an average molecular weight of 15,000, hydrochloric acid (37%), pyrrole, glutaraldehyde (50% aqueous solution), poly(ethylene glycol) diacrylate [number-average molecular weight (Mₙ), ~700], chitosan with low molecular weight, 2,2′-azobis(2-methylpropionitrile), and ammonium persulfate were purchased from Sigma-Aldrich. All the materials were used without further purification.

Preparation of h-LAHs
In a typical synthesis, PPy (100 μl, 10 wt %) solution and glutaraldehyde [12.5 μl, 50 wt % in deionized (DI) water] were added to 1 ml of PVA/chitosan precursor solution. The gelation was carried out for 24 hours. The obtained gel was immersed into DI water overnight to obtain the pure hydrogel. The purified hydrogel 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. Last, the obtained hydrogel sample was fully swollen for testing.

SVG experiments
The water evaporation performance experiments were conducted using a solar simulator (M-LS Rev B, Abet Tech), outputting a simulated solar flux of 1 sun. The solar flux was measured using a thermopile (818SL, Newport) connected to a power meter (1916-R, Newport). h-LAHs with a thickness of ca. 0.5 cm were floated on pure water (or unpurified for purification tests) in a beaker with a solar flux of 1 sun. The mass of the water loss was measured by a lab balance with a 0.1-μg resolution and calibrated to weights heavier than the total weight of the setup. All evaporation rates were measured after a stabilization under 1 sun for 30 min.
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Sci Adv 5 (6), eaaw5484.
DOI: 10.1126/sciadv.aaw5484