Localized Heating by a Photothermal Polydopamine Coating Facilitates a Novel Membrane Distillation Process

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Localized Heating by a Photothermal Polydopamine Coating
Facilitates a Novel Membrane Distillation Process

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ABSTRACT

Solar-driven membrane distillation using photothermal membranes is of considerable interest for future water desalination systems. However, the low energy efficiency, complex synthesis, and instability of current photothermal materials hinder their further development and practicability. In this study, for the first time, we demonstrate a simple, stable, and scalable polydopamine (PDA) coated polyvinylidene fluoride (PVDF) membrane for highly efficient solar-driven membrane distillation. Our membrane shows the best energy efficiency among existing photothermal membranes (45%), and the highest water flux (0.49 kg/m²·h) using a direct contact membrane distillation (DCMD) system under 0.75 kW/m² solar irradiation. Such performance was facilitated by the PDA coating, whose broad light absorption and outstanding photothermal conversion properties enable higher transmembrane temperature and increased driving force for vapor transport. In addition, the excellent hydrophobicity achieved by fluoro-silanization gives the membrane great wetting resistance and high salt rejection. More importantly, the robustness of our membrane, stemming from the excellent underwater adhesion of the PDA, makes the composite membrane an outstanding candidate for real-world applications.
Rapidly increasing population, economic development, and water contamination have resulted in unprecedented global fresh water demands. To augment the freshwater supply and alleviate water scarcity, desalination of seawater and brackish water, which comprise 97.5% of the total water on earth, has been extensively implemented by many countries in the past few decades. Over 19,000 water desalination plants have been built globally, reaching an estimated capacity of 100 million m³/day by 2017. Water desalination technologies include those without phase change processes, such as reverse osmosis (RO) and electrodialysis (ED), and those that involve phase change processes, such as thermal distillation (i.e., boiling) and membrane distillation (MD).

Membrane distillation, an advantageous thermally-driven membrane technology, generates clean water based on the vapor pressure difference between the two sides of a porous hydrophobic membrane. In direct contact membrane distillation (DCMD), the most common MD configuration, water evaporates on the hot feed water side of the membrane surface, diffuses across the microporous membrane, and condenses on the cold distillate side. MD can be operable under conditions with lower temperatures than boiling and lower pressures than RO, leading to decreased electricity input and less fouling or corrosion problems. Moreover, less sophisticated equipment and pretreatment systems facilitate MD to possess small footprint, compactness, and high modularity. The use of renewable energy sources to heat feed saline water, such as waste heat from power plants and solar energy by implementing solar thermal collection systems, further incentivizes MD’s application for sustainable water desalination. However, one of the main challenges of conventional MD is temperature polarization, which results in a lowered surface temperature at the membrane-feed water interface with respect to its bulk water value. Consequently, the cross-membrane
temperature difference is decreased, reducing the driving force for mass transport and undermining the overall MD performance.\textsuperscript{33}

Most recently, light-driven localized heating at membrane surfaces that incorporate photothermal materials (e.g., Ag nanoparticles, carbon black, and nitrocellulose) has provided a means to alleviate the concerns brought by the influence of temperature polarization.\textsuperscript{33-35} With the integration of photothermal materials, localized heating can be efficiently generated from incident light (especially, renewable solar irradiation), which helps to increase and maintain the membrane surface temperature at the membrane-feed water interface. The MD system using photothermal membranes can significantly reduce the electricity input, while possessing other advantages of conventional MD processes such as less fouling problems and the modularity to combine with other systems.\textsuperscript{18} However, the photothermal materials demonstrated so far have several limitations which hinder their further development and commercial practicability. For example, Ag nanoparticles are prone to delamination or leakage from membranes into water.\textsuperscript{33} The dissolution of photothermal material will restrict its utilization for certain MD configurations (e.g., vacuum membrane distillation), and also lead to the potential impairment of the membrane’s photothermal performance during long term applications. On the other hand, the bilayer structure of carbon black coating on the membrane surface makes the carbon black membrane exhibit low photothermal conversion efficiency.\textsuperscript{34} Besides, the synthesis methods of these composite membranes are often complex, involving phase inversion or electrospinning processes, which may be cost and energy intensive.

Herein, we demonstrate, for the first time, a simple, stable, and highly effective PDA coated polyvinylidene fluoride (PVDF) membrane for solar-driven membrane distillation. Polydopamine, as a mussel-inspired polymer,\textsuperscript{36} has been extensively applied in surface
Polydopamine can be easily coated on surfaces, regardless of their initial surface energy, making the synthesis simple and cost-effective. The PDA coating on organic substrates is extremely stable under harsh conditions, including ultrasonication or acidic pH (<1), which makes the long-term commercial application of PDA-coated materials viable. Similar to those of naturally occurring eumelanin, PDA also exhibits broad light absorption and remarkable photothermal conversion properties, which ensures its potential application for highly efficient solar-based seawater desalination. Moreover, the biocompatibility, low toxicity and biodegradable nature of PDA make it an environmentally benign material for water purification and biomedical applications. Previously, PDA has been applied for seawater desalination techniques, such as forward osmosis and nanofiltration, to increase the permeate flux facilitated by only exploiting its hydrophilic nature. However, there is still plenty of room to utilize PDA for solar-driven seawater desalination applications considering its superb photothermal properties, especially in solar-driven membrane distillation. The solar-driven MD system using PDA in this study shows the best thermal efficiency to date among currently reported photothermal MD systems, and the highest water flux using a DCMD system among currently reported solar-driven MD studies. The simple, stable, and highly effective photothermal membrane introduced in this study can help to expand PDA’s application and provide a promising option to alleviate the global fresh water scarcity problems.

Polydopamine coating on a commercial hydrophilic PVDF membrane (0.45 µm pore size; MilliporeSigma) can be easily achieved via a self-polymerization process (Fig. 1A and Fig. S1, ESI†). The PVDF membrane has been widely used for MD systems, and in our work, hydrophilic PVDF was chosen to achieve easier and more efficient PDA coating owing to PDA’s...
hydrophilic nature. With 2 mg/mL dopamine (DA) in 10 mM Tris-HCl (pH 8.5) solution, the self-polymerization process was repeated for 7 days to ensure that the entire surface of the PVDF was uniformly coated by PDA (Fig. S1). The uniformity coating of PDA on PVDF surface can minimize the influence of light illumination spot on the membrane’s photothermal reactivity. The amount of PDA coating can be tuned by varying the number of coating cycles, and the final weight percentage of PDA on PVDF after 7 cycles was quantified to be 9.7±0.5 wt% by measuring the weight difference of the membrane before and after polymerization. With the additional coating of PDA, the porosity (ε) of the PDA-PVDF membrane decreased slightly (73.2% ± 2.6%, compared with 82.1% ± 4.2% for a pristine PVDF membrane, measured by a gravimetric method).\textsuperscript{53-55} Hydrophobicity is important for MD membranes because it resists pore wetting, ensures the passage of only the vapor phase through the membrane pores, and enhances the salt rejection performance of the membrane.\textsuperscript{20} The hydrophobicity of PDA-coated PVDF membrane was increased by a facile fluoro-silanization method using (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane (FTCS),\textsuperscript{56, 57} leading to a water contact angle of 125.5º. The above processes are evident in a morphological investigation carried out by scanning electron microscopy (SEM) and contact angle measurements, which clearly show a uniform and dense coating of PDA on the microporous PVDF surface and cross-section (Fig. 1B-G), and the successful hydrophobic modification of FTCS, respectively (inset in Fig. 1A). ImageJ analysis of surface SEM images (×5000 magnification) indicates that an average surface pore size of FTCS-PDA-PVDF membrane was 0.96 ± 0.42 µm by taking measurements of 100 pores.\textsuperscript{58, 59} The average pore size of FTCS-PDA-PVDF membrane became larger compared with pristine PVDF membrane (0.46 ± 0.13 µm, confirmed by SEM images), which can be due to the fact that the PDA coating closed the smaller pores rather than the bigger pores, making the average pore size
increase (Fig. 1B and 1E). Consequently, the pore numbers calculated from SEM images also decreased from $2.6 \times 10^7$/cm$^2$ of pristine PVDF membrane to $1.1 \times 10^6$/cm$^2$ of FTCS-PDA-PVDF membrane.

To further understand the chemical composition of the synthesized FTCS-PDA-PVDF membrane, we have performed attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy measurements (Fig. 2A). The characteristic N-H and C=C peaks of PDA on PVDF at 1520 and 1610 cm$^{-1}$, and the Si-O peak of FTCS at 1010 cm$^{-1}$, respectively indicated the successful coating of PDA and the FTCS modification. The ATR-FTIR reference peaks for PDA coating on PVDF are summarized in Table S1†. Raman spectroscopy also showed peaks of PDA at 1350 and 1573 cm$^{-1}$ (Fig. S2A†), corresponding to the stretching and deformation of PDA’s catechol groups. X-ray photoelectron spectroscopy (XPS) revealed the chemical composition difference between pristine PVDF and FTCS-PDA-PVDF, based on the N 1s, Si 2p, and C 1s peaks (Fig. 2B–D). As shown in Fig. 2B, a new N 1s peak emerged at 398–402 eV for the FTCS-PDA-PVDF, corresponding to the N-C and N-H bonds of PDA layers on the surface of PVDF membrane. The new emerging Si 2p peak of FTCS-PDA-PVDF at 103.8 eV (Fig. 2C) showed the Si-O bond of FTCS on the PDA-PVDF surface. Within the broad C 1s peak (Fig. 2D), the increased relative ratio of –CF$_2$– (290.2 eV) over –CH$_2$– (285.2 eV) and the newly appeared –CF$_3$ peak (292.3 eV) from FTCS-PDA-PVDF were attributed to the fluorinated tails of FTCS on the PVDF surface. Further, to evaluate the PDA coating effects on surface roughness, the root-mean-square (RMS) roughnesses of both FTCS-PDA-PVDF (179 ± 12 nm) and pristine PVDF (498 ± 31 nm) membranes were acquired by measuring tapping mode atomic force microscopy (AFM) images (Fig. S2B†). The lowered surface roughness after PDA coating
can be attributed to the partial filling of large pores in the PVDF membrane with PDA, which can also be observed in SEM images.

In light-to-heat conversion by photothermal materials, the light absorption properties are of crucial importance. Hence, following the chemical characterization, the transmittance and reflectance measurements of the FTCS-PDA-PVDF membrane were carried out in the range of 450–800 nm, using a micro-spectrophotometer (Fig. 3A and 3B, and the ESI†). The light absorption properties of pristine PVDF membranes modified only by FTCS (FTCS-PVDF) and by PDA (PDA-PVDF) were also measured for comparison. The FTCS-PVDF membrane showed high transmittance (~17.1%) and reflectance (~27.6%) in the visible region, which indicated relatively low light extinction (~55.3%). On the other hand, after PDA coating, the PDA-PVDF and FTCS-PDA-PVDF membranes exhibited extremely small optical transmittance (~0.4% for PDA-PVDF, and ~0.1% for FTCS-PDA-PVDF) and reflectance (~2.6% for PDA-PVDF, and ~3.7% for FTCS-PDA-PVDF) in the visible region, indicating a large optical extinction (~97.0% for PDA-PVDF, and ~96.2% for FTCS-PDA-PVDF) by the membrane. This excellent light extinction property, which was mainly attributed to light absorption by the PDA coating and light scattering by the membrane’s porous structure, underlies the light-to-heat conversion of the FTCS-PDA-PVDF membrane.

Further, to probe the photothermal conversion performance of the FTCS-PDA-PVDF membrane, the surface temperatures of dry FTCS-PVDF, PDA-PVDF, and FTCS-PDA-PVDF were measured by an infrared (IR) camera under light illumination from a solar simulator (Fig. 3C and 3D). Two light intensities were used to represent unfocused and focused illumination, and the power densities were measured to be 0.75 (~0.7 sun) and 7.0 kW/m² (~7 sun) respectively by a spectroradiometer (Fig. S3†). After 600 secs illumination, the surface
equilibrium temperature of dry FTCS-PDA-PVDF increased from room temperature (20 ºC) to 35 ºC (at 0.75 kW/m²) and to ~97 ºC (7.0 kW/m²). The surface temperature of the dry PDA-PVDF membrane also increased from 20 ºC to ~35 ºC (0.75 kW/m²) and to ~96 ºC (7.0 kW/m²).

In comparison, the dry FTCS-PVDF membrane surface temperature increased only from 20 ºC to ~23 ºC (0.75 kW/m²) and to ~27 ºC (7.0 kW/m²) under the same irradiation conditions. To evaluate the photothermal conversion properties of the membranes under water, the surface temperatures of membranes with water on top (8 mm distance from the membrane to the air/water interface) were also monitored using a benchtop controller thermocouple probe. For membranes immersed in water, the temperature increases on the top of the membrane surface were smaller than those of dry membranes. Under water, after 600 sec illumination, the surface equilibrium temperature of FTCS-PDA-PVDF membrane increased from 20 ºC to ~26 ºC (0.75 kW/m²) and to ~32 ºC (7.0 kW/m²), and the temperature of PDA-PVDF membrane increased from 20 ºC to ~25 ºC (0.75 kW/m²) and to ~31 ºC (7.0 kW/m²), while the temperature of FTCS-PVDF membrane increased only from 20 ºC to ~22 ºC (0.75 kW/m²) and to ~24 ºC (7.0 kW/m²).

The water on top of the membrane absorbed and scattered photons passing through, thus reducing the number of photons absorbed by the PDA coating on the membrane. The above results confirmed that the PDA coating on the PVDF surface exhibited high photothermal conversion and can be utilized for localized heating under solar irradiation.

The solar-driven membrane distillation performance of the FTCS-PDA-PVDF membrane was tested in a specially designed direct contact membrane distillation (DCMD) module (Fig. 4A and Fig S4†). The distillate (DI water, 20 ºC) was circulated with a flow rate of 16.2 mL/min, and the increasing weight of the distillate was measured continuously by a balance to quantify the amount of collected water. To test the membrane distillation performance within 60 minutes
(Fig. 4B and 4C) under different salinities, both pure water and highly saline water (0.5 M NaCl) were used as feed water (20 °C) with a flow rate of 3.6 mL/min. Here, the 0.5 M salinity was chosen to mimic the average salinity of seawater.\textsuperscript{71} The FTCS-PVDF membrane was used as a control membrane for comparison. For the FTCS-PDA-PVDF membrane with pure water, the water flux was 0.58 kg/m\textsuperscript{2}\cdot h under 0.75 kW/m\textsuperscript{2} irradiation. On the other hand, for the FTCS-PVDF membrane, the water flux was only 0.12 kg/m\textsuperscript{2}\cdot h under identical irradiation, which is 3.8 times lower than that of the FTCS-PDA-PVDF membrane. With higher irradiation intensity (7.0 kW/m\textsuperscript{2}), the water flux of the FTCS-PDA-PVDF membrane increased to 5.17 kg/m\textsuperscript{2}\cdot h, 12.6 times higher than that of FTCS-PVDF membrane (0.38 kg/m\textsuperscript{2}\cdot h) under identical irradiation. In comparison, the water flux collected with saline feed water was lower than that of pure water for both the FTCS-PVDF and FTCS-PDA-PVDF membranes. The water fluxes for the FTCS-PDA-PVDF membrane were 0.49 and 4.23 kg/m\textsuperscript{2}\cdot h under 0.75 and 7.0 kW/m\textsuperscript{2} irradiations, significantly higher than those of the FTCS-PVDF membrane (0.09 and 0.22 kg/m\textsuperscript{2}\cdot h). The lower water flux with saline water was due to the lower vapor pressure being in equilibrium with the feed, resulting in a lower vapor pressure difference across the membrane.\textsuperscript{72, 73} To put the FTCS-PDA-PVDF membrane in real-world use perspective, with saline water, a permeate flux rate of ~0.49 kg/m\textsuperscript{2}\cdot h, and an active area of \(~1 \times 1\) m\textsuperscript{2}, our solar MD system could generate 3.92 L/day under 0.75 kW/m\textsuperscript{2} irradiation, with 8 h of sunlight time and at \(~20\) °C ambient temperature. This outstanding solar-driven MD performance of the FTCS-PDA-PVDF membrane makes it highly attractive for efficient and sustainable desalination process.

The feed flow rate is crucial for MD efficiency because it affects the heat transfer in the feed channel and the temperature polarization effects on the membrane surface.\textsuperscript{19} Therefore, to evaluate the influence of feed flow rate on the solar-driven MD performance, we also measured
the permeate water flux with varied feed flow rates (1.5–8.1 mL/min) for FTCS-PDA-PVDF membranes (Fig. 4D, Fig. S5†) with simulated solar irradiation. The tests were conducted in triplicate, using a new membrane each time. With 0.75 kW/m² irradiation, the fluxes with pure water and saline water decreased from 0.66 and 0.57 kg/m²·h to 0.49 and 0.43 kg/m²·h, respectively, when the feed flow rate increased from 1.5 to 8.1 mL/min. With 7.0 kW/m² irradiation, the fluxes with pure water and saline water decreased from 5.89 and 4.87 kg/m²·h to 4.18 and 3.51 kg/m²·h, respectively (Fig. S5A-B†). As shown in the schematic diagram comparing conventional MD and solar-driven MD in Fig. S5C†, for conventional MD systems, the permeate water flux increases with an increasing feed water flow rate, owing to better mixing in the flow channel and decreased temperature polarization effects. Contrarily, in the solar-driven MD system, the permeate water flux decreased with increasing feed water flow rate. With higher feed flow rate, the heat loss from the heated membrane top surface to the bulk feed water was faster, leading to a smaller temperature gradient across the membrane. Similar trends have been reported in a recent study using carbon black as photothermal material. However, with feed flow rates of 1.5–8.1 mL/min and irradiation of 0.75 kW/m², the permeate flux with saline feed water (0.5 M NaCl) of our membrane (0.43–0.57 kg/m²·h) was about twice as high as that reported for the carbon black membrane (~0.21–0.27 kg/m²·h) under similar conditions.

The solar conversion efficiency (η), which describes the overall membrane thermal efficiency, was defined as the ratio of the energy needed to generate permeate flux over the total energy input by solar irradiation (I, kJ/m²·h) (same as the gained output ratio, see detailed description in the section S4 in ESI†). The energy needed for permeate flux was calculated by multiplying the permeate flux (ṁ, kg/m²·h) by the evaporation enthalpy change (H_{\text{vap}}, 2,454 kJ/kg) of water. As shown in Fig. 4E, with a pure water flow rate of 3.6 mL/min, the solar...
conversion efficiency of the FTCS-PDA-PVDF membrane was calculated to be 53% under 0.75 kW/m$^2$ irradiation, much higher than the 10% of FTCS-PVDF under identical irradiation. When the feed flow rates were adjusted from 1.5 to 8.1 mL/min, the solar efficiencies decreased from 60% to 44%. At a flow rate of 3.6 mL/min with saline water, the solar conversion efficiencies of FTCS-PDA-PVDF membranes were 45% and 41% under 0.75 and 7.0 kW/m$^2$ irradiations, respectively. For both pure water and saline water, the solar efficiencies decreased when using larger feed flow rates. Previous studies have used silver nanoparticles, nitrocellulose, and carbon black as photothermal materials for light-driven MD systems with excellent flux penetration and solar conversion efficiencies. However, our FTCS-PDA-PVDF membrane exhibited even higher solar conversion efficiency (45% for saline water under 0.75 kW/m$^2$ irradiation) than membranes using silver nanoparticles (36.9%), nitrocellulose (31.8%) and carbon black (21.5%) (Table S2†). The outstanding solar conversion efficiency of the FTCS-PDA-PVDF membrane compared with other recently reported membranes can be mainly attributed to three factors: (i) The superior light absorption properties of PDA. Polydopamine has wider light absorption range than Ag nanoparticles, which absorb light mainly in the UV range. (ii) The high surface temperature on the top of membrane owing to the excellent photothermal conversion properties of PDA, even with a thick water layer on top of the membrane surface. PDA is known to convert 99% of the absorbed photon energy into heat within 50 ps. (iii) The high density and uniformity of the PDA coating on the PVDF membrane surface as shown in SEM images. The uniform self-polymerization of dopamine and the excellent adhesion of PDA to a multitude of surfaces foster ‘proximal’ photothermal conversion activity. Such proximal photothermal conversion leads to an increased transmembrane temperature and a larger vapor pressure difference across the membrane. In contrast, in the previous work using a carbon black
layer on top of the PVDF membrane, the light-absorbing layer is far from the PVDF membrane surface, decreasing the transmembrane temperature and the driving force for vapor transport.\textsuperscript{34}

In terms of solar conversion efficiency, although our membrane achieved the highest efficiency among existing photothermal MD membranes, it is relatively lower than those of photothermal steam generation membranes.\textsuperscript{41, 75, 76} The main reasons behind the lower efficiency in photothermal MD are the top water layer interference and conductive heat loss. With water thickness ranging from 1.5–8 mm in existing photothermal MD systems (Table S2†), this top water layer can reduce the number of photons absorbed by the photothermal membrane and thus lead to a lower membrane surface temperature. In addition, the floating feed water system further increases the conductive heat loss, while for photothermal steam generation, the untreated water under the evaporators is often in a stagnant system. Although the efficiencies of current photothermal steam generation are higher, the steam collection still remains as the challenge before its large scale applications. In the future, efforts should be put into increasing the solar conversion efficiency of photothermal MD by developing new MD modules or membranes to exalt its competitiveness among all the photothermal desalination techniques. Furthermore, photothermal MD can be more advantageous when it is used for flowback water treatment from unconventional oil and gas recovery systems, which already contain high temperature water (e.g., \textasciitilde60–70 °C).\textsuperscript{77} The high temperature feed water along with photothermal temperature rise, makes the overall MD process more efficient.

The chemical and mechanical stability of the FTCS-PDA-PVDF membrane was investigated further by subjecting it to both ultrasonic agitation for 6 hours and vigorous shaking for 30 days at three pH values (pH 4, 7, and 10) (Fig. S6A†). Even after these extreme stress tests, the FTCS-PDA-PVDF membrane did not exhibit discernible signs of disintegration or loss.
of PDA coating from the surface. The morphology of the FTCS-PDA-PVDF membrane remained unaltered after 10 cycling tests with pure water and saline water, as shown by the SEM images of the FTCS-PDA-PVDF membrane surface (Fig. S6B-C†). Then, to evaluate the potential changes in membrane wetting after several MD cycles, the contact angles of pure water and saline water on the membrane were measured (Fig. S6D†). For an unused FTCS-PDA-PVDF membrane, the contact angles were 125.5º ± 1.9º and 126.1º ± 1.6º for pure water and saline water, respectively. After 10 cycles of MD tests (1 hr × 10 times), the contact angles for pure water and saline water were 124.3º ± 1.5º and 125.4º ± 1.3º, indicating less than 1% variation in the contact angle. Pore wetting problems have constrained the use of many MD membranes for long term or large scale applications. However, the excellent and stable hydrophobicity of the FTCS-PDA-PVDF membrane, owing to the covalent and dense FTCS fluoro-silane, confers long-lasting and stable wetting resistance. The variation of membrane mass was also smaller than 1% over 10 cycles of MD tests using saline water with focused irradiation (7.0 kW/m²) (Fig. S6E†). The salt rejection was larger than 99.9% over 10 cycles of MD tests using saline water under both unfocused (0.75 kW/m²) and focused (7.0 kW/m²) irradiations (Fig. S6E†). This high salt rejection of FTCS-PDA-PVDF membrane can be attributed to the operation conditions of the DCMD (low hydrostatic pressure), and to the excellent hydrophobicity and wetting resistance of the membrane. Furthermore, the flux performance of FTCS-PDA-PVDF membrane remained stable over 10 cycles of MD tests (less than 5% variation, Fig. S6F†). The remarkable chemical and mechanical stability of the FTCS-PDA-PVDF membrane, owing to the strong adhesion between PDA and the PVDF surface, can lessen environmental concerns or the need for further treatment caused by the possible
detachment of photothermal materials from the membrane surface, and increase the longevity of membranes for long term solar MD applications.

In summary, we present a simple, stable, and highly effective photothermal membrane for solar-driven membrane distillation. Owing to the remarkable light absorption and outstanding photothermal conversion properties of the PDA coating, the FTCS-PDA-PVDF membrane exhibited excellent solar membrane distillation performance (efficiency of 45% under 0.75 kW/m$^2$ irradiation). The FTCS-PDA-PVDF membrane exhibited a 4.23 kg/m$^2$·h permeate flux under 7.0 kW/m$^2$ irradiation, a 19-fold enhancement over FTCS-PVDF membrane. In addition, the proximal polymerization process that leads to strong adhesion between PDA and the PVDF surface resulted in the excellent chemical and mechanical robustness and stability of the FTCS-PDA-PVDF membrane, which allows its utilization in long term solar MD applications. In comparison with recently reported photothermal membranes which utilized phase inversion or electrospinning processes, PDA polymerization would be a much easier way to achieve proximal photothermal conversion activity. The simplicity of the PDA coating method also makes the membrane attractive for future commercial applications. From engineering perspectives, with built-up systems with multiple industrial-scale tanks, the final coated-membrane area can be significantly larger than other existing membrane modification methods to achieve a similar extent of photothermal performance. In the future, efforts can be put into expediting the PDA polymerization by optimizing the reaction conditions and designing better mixing systems. Coupled with renewable and sustainable solar irradiation, the highly efficient photothermal membrane introduced here can provide a promising option to alleviate the global water crisis.

Conflicts of interest
There are no conflicts to declare.

Acknowledgments

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List of Figures

Fig. 1  (A) Schematic depicting the synthesis of the FTCS-PDA-PVDF membrane. SEM images of the pristine PVDF membrane surface (B and C) and cross-section (D). SEM images of the FTCS-PDA-PVDF membrane surface (E and F) and cross-section (G).

Fig. 2  Characterization of the FTCS-PDA-PVDF membrane. (A) ATR-FTIR spectra of the pristine PVDF and the FTCS-PDA-PVDF membranes. XPS spectra of the pristine PVDF and the FTCS-PDA-PVDF membranes showing the N 1s (B), Si 2p (C), and C 1s (D) peaks.

Fig. 3  Optical and thermal properties of the FTCS-PDA-PVDF membrane. (A) Transmittance and (inset) reflectance spectra of the FTCS-PVDF, PDA-PVDF, and FTCS-PDA-PVDF membranes. (B) Light extinction spectra of the FTCS-PVDF, PDA-PVDF, and FTCS-PDA-PVDF membranes. (C) IR camera images of the FTCS-PVDF membrane under illumination of 7.0 kW/m$^2$ (i), 0.75 kW/m$^2$ (iv), the PDA-PVDF membrane under illumination of 7.0 kW/m$^2$ (ii), 0.75 kW/m$^2$ (v), and the FTCS-PDA-PVDF membrane under 7.0 kW/m$^2$ (iii), and 0.75 kW/m$^2$ vi) after 600 sec illumination. (D) Surface temperature increase ($\Delta T$, °C) from room temperature (20 °C) of the FTCS-PVDF, PDA-PVDF, and FTCS-PDA-PVDF membranes, after 600 sec illumination at 7.0 kW/m$^2$ and 0.75 kW/m$^2$, both under dry conditions and under water (water thickness = 8 mm).

Fig. 4  (A) Schematic depicting the solar-driven DCMD system. Collected water (kg/m$^2$) using the FTCS-PVDF and the FTCS-PDA-PVDF membrane using both pure water (B) and 0.5 M NaCl saline water (C) under different solar irradiations. Flux (D) and
efficiency (E) of solar-driven DCMD system using the FTCS-PDA-PVDF membrane with varying feed flow rates, using both pure water and 0.5 M NaCl saline water under different solar irradiations. Triplicate membrane samples were tested in all cases.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
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This study demonstrates a simple, stable, and scalable polydopamine (PDA) coated PVDF membrane for highly efficient solar-driven membrane distillation.