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Freshwater production by solar desalination of seawater using two-ply dye modified membrane system

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ABSTRACT

Freshwater production from seawater using solar energy is now an essential technology as a countermeasure of global water shortage. We have previously reported a seawater desalination process by membrane permeation of the water. In this process, seawater put on dye modified hydrophobic membrane is vaporized by irradiated light with the modified dyes. The water vapor thus formed penetrates through the membrane, and desalinated water is recovered under the membrane. This paper reports our latest approaches to enhance the performance of the solar desalination of seawater by the membrane permeation. Solvent black 5 (SB5) that absorbs the wide range of sunlight including near-infrared light was effective as a dye used for the desalination process. For scaling-up this process, dye modified membranes were tightly sandwiched between two flanges for holding a large volume of seawater on the membrane. The two-ply membrane system consisting of SB5 modified cellulose membrane on non-modified polytetrafluoroethylene membrane was found to be the best combination for freshwater production from seawater by the irradiation of simulated sunlight. Desalination of actual seawater using natural sunlight was also achieved by the two-ply membrane system. These results indicated that the freshwater production by the solar desalination of seawater with the membrane permeation is a practical countermeasure for global water shortage.

Keywords: Desalination of seawater; Solar energy; Freshwater production; Dye modified membrane; Membrane permeation

1. Introduction

Freshwater production from seawater as an unlimited water source is a strong countermeasure for global water shortage [1–5]. Since the water shortage is assumedly related to global warming (global climate change) that arises from the emission of CO_2 from fossil fuels, freshwater production should be free from the consumption of the fuels [4]. Seawater desalination through distillation by heating seawater is a simple approach that can desalinate even high salinity saltwater, which is unmanageable by reverse osmosis (RO) process [5]. However, the distillation process requires larger amounts of energy due to the high vaporization heat of the water. Recently, the application of solar energy to the seawater desalination ("solar desalination") is highlighted for building a sustainable society [6–11], because the utilization of solar energy causes no CO_2 emissions. Moreover, since serious water shortage is observed in many different areas all over the world, the direct use of solar energy in each place is more appropriate for freshwater production. Especially in regions having only untreated raw water and sunlight, the desalination process using simple apparatuses is more appropriate.

A typical simple process of freshwater production by the direct use of solar energy is solar still [12–15], where raw seawater stored in a water pool with light-harvesting materials

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is exposed to sunlight for evaporation. In a typical apparatus, water vapor thus formed is condensed on the undersurface of a transparent plate placed above the water pool and is collected in an attached drain as desalinated water. Therefore, for efficient recovery of the evaporated water, some specific installations are required for solar still. Recently solar thermal desalination of seawater is actively studied using photothermal materials [16–26]. These materials are designed for the efficient conversion of light energy to heat generation. Although water vapor is effectively produced from seawater under the irradiation of simulated sunlight using these materials, seawater is simply evaporated and the water vapor is not recovered in most studies [20–24]. For collecting the water vapor, the condensation treatment using a transparent plate located above the photothermal materials, which is analogous to solar still, is necessary. This recovery process naturally needs some particular installations for the condensation and the collection of water vapor. On the other hand, a membrane distillation (MD) process combining with solar thermal devices is reported to be advantageous even for collecting water vapor [25,26]. We also reported a simple and compact process of water purification and seawater desalination using light energy [27–29] by an analogous mechanism of air-gap MD process [30–32]. In this process, seawater put on a dye modified hydrophobic membrane is directly exposed to an irradiated light. The dye modified to the membrane absorbs the light to generate heat and evaporate the water. Water vapor thus produced penetrates through the membrane. By the condensation of the vapor under the membrane, purified and desalinated water is obtained. A schematic diagram of seawater desalination by our membrane permeation is illustrated in Fig. 1. This process is different from common MD in that raw seawater at ordinary temperature can be directly used. The desalinated water is easily collected in a container placed under the membrane, while solar still requires some mechanisms for recovering condensed water above seawater [12–15]. On the other hand, our apparatus used in previous papers [27–29] can treat <1 mL of water, which is extremely low volume for practical freshwater production. As it is reported that the daily requirement of drinking water for one adult is assumed to 1.5 L [33], we wish to improve our process to a larger scale.

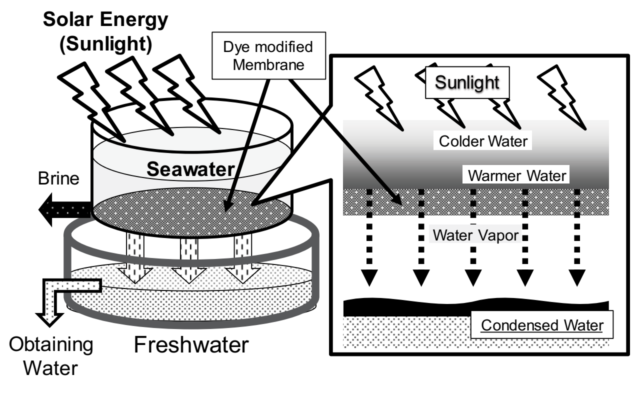

Fig. 1. A schematic diagram of solar desalination of seawater by membrane permeation with dye modified membrane using sunlight.

In this paper, we report our latest approaches to enhance the performance of the solar desalination of seawater by the membrane permeation with dye modified membranes. At first, we used a more effective dye (solvent black 5) that absorbs the wide range of sunlight including near-infrared light [34], and the improvement of the apparatus is attempted with this new dye. We next examined a two-ply membrane system consisting of a dye modified hydrophilic membrane and a non-modified hydrophobic one for freshwater production from seawater using solar energy. The comparison of our process with solar still is also discussed. Finally, the desalination of actual seawater using natural sunlight was addressed by the two-ply membrane system.

2. Materials and methods

2.1. Materials

Polytetrafluoroethylene (PTFE) membranes used in this study were PTFE membrane filters (diameter: 47 mm and 90 mm, thickness: 0.075 mm, and pore size: 3.0 μm) and PTFE filter paper (PF050; diameter: 55 mm, thickness: 0.36 mm, and retained particle diameter: 5 μm) purchased from Toyo Roshi Kaisha (ADVANTEC), Tokyo, Japan. Cellulose membrane was a filter paper of Kiriyama glass CO. (No. 5A; diameter: 40 mm, retained particle diameter: 7 μm). Disperse red 1 [DR1; N-ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline] and disperse blue 14 [DB14; 1,4-bis(methylamino)anthraquinone] were obtained from Sigma-Aldrich Japan (Tokyo, Japan). Solvent black 5 (SB5) was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. The molecular structures of DR1 and DB14 are shown in our previous paper [29], and that of SB5 is illustrated in Fig. 2. Other reagents were purchased from FUJIFILM Wako Pure Chemical Corporation, (Osaka, Japan). Artificial seawater was prepared by mixing MARINE ART SF-1 (Osaka Yakken Co., Ltd., Mino, Japan) with an appropriate volume of distilled water [35]. The contents of dissolved ions in the artificial seawater are as follows; NaCl: 22.1 g/L, $MgCl_2·6H_2O$: 9.9 g/L, $CaCl_2·2H_2O$: 1.5 g/L, Na_2SO_4: 3.9 g/L, KCl: 0.61 g/L, $NaHCO_3$: 0.19 g/L, KBr: 96 mg/L, $Na_2B_4O_7·10H_2O$: 78 mg/L, $SrCl_2$: 13 mg/L, NaF: 3 mg/L, LiCl: 1 mg/L, KI: 81 μg/L, $MnCl_2·4H_2O$: 0.6 μg/L, $CoCl_2·6H_2O$: 2 μg/L, $AlCl_3·6H_2O$: 8 μg/L, $FeCl_3·6H_2O$: 5 μg/L, $Na_2WO_4·2H_2O$: 2 μg/L, $(NH_4)_6Mo_7O_{24}·4H_2O$: 18 μg/L. Saturated seawater was obtained as a supernatant solution of the mixture with a large amount of MARINE ART SF-1 (8 times) and distilled water. Actual seawater was collected at Sanriku seacoast of Okatsu-cho of Ishinomaki city (northern latitude of about

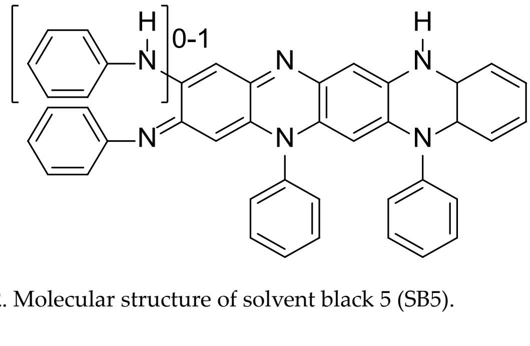

Fig. 2. Molecular structure of solvent black 5 (SB5).

38.5° and east longitude of about 141.5°), and this seawater was used for desalination experiments after simple natural filtration for removing insoluble matters.

2.2. Preparation procedures of dye modified membranes

Dye modified PTFE membranes were obtained by the following procedures [29]. A PTFE membrane was immersed in acetone solution of SB5 (0.01 g/mL) for 10 min and the membrane was picked up from the solution. After heating at 50°C for 10 min in air, the membrane was soaked in the dye solution again with flipping the membrane upside down. After 10 min of the immersion, the membrane was heated again at 50°C for 10 min. These procedures were repeated a totally of 10 times. The resulting membrane was immersed in 500 mL of distilled water overnight and was finally treated by ultrasonic cleaning in distilled water. After drying at 50°C, the membrane thus obtained was used for experiments. PTFE membranes modified with DR1 or DB14, and DR1–DB14 double-modified PTFE membrane were newly prepared in this study by the same procedures as SB5 modified one.

SB5 modified cellulose membrane was obtained by spreading 0.1 mL of DMF (N,N-dimethylformamide) solution of SB5 (0.01 g/mL) to the whole cellulose filter paper. After heating at 150°C for 1 h in air, the DMF solution (0.1 mL) was spread to the backside of the paper and heated again at 150°C for 1 h. Finally, the DMF solution (0.1 mL) was applied to the front side again, and heated at 150°C for 1 h. The following washing treatments were similar to those of dye modified PTFE membranes mentioned above.

2.3. Experiments of membrane permeation of water

The experiment of the membrane permeation of water with the petri dish system was carried out with the same apparatus used in our previous papers basically [27–29]. In this study, an O-ring made of PTFE was put on a PTFE membrane (membrane filters; diameter: 47 mm) for avoiding the spilling of the water (Supplementary information S1). Simulated sunlight was irradiated to the whole PTFE membrane with 0.5 mL of water drop using a solar simulator (Solar Simulator XEF-300, SAN-EI ELECTRIC Co. Ltd., Osaka, Japan) at the intensity of 1,000 W/m^2 (1 SUN) for 30 min. The intensity was fixed using a pyranometer (ML-01 Sipyranometer, EKO instruments, Tokyo, Japan). The distance from the lamp bottom to the membrane was ~225 mm. After the light irradiation, waters obtained on the undersurface of a glass plate placed at the upper side of the membrane and on the upper surface under the membrane were recovered with a microsyringe to measure their volumes.

In the experiment of the membrane permeation using flange system, a dye modified PTFE membrane (PTFE filter paper PF050; diameter: 55 mm) was directly sandwiched between two plastic flanges (a slip-on type; in one flange, outer diameter: 115 mm, inner diameter: 42 mm, thickness: 14 mm), and these two flanges were tightly bolted as illustrated in Fig. 3a. On the top and the bottom of the connected two flanges, borosilicate glass plates were set for recovering condensed waters (Fig. 3b). Distilled water or seawater was slowly poured into the cylindrical space from the upper side of the flanges. The simulated sunlight was irradiated to the whole part of the cylindrical space of the connected flanges at the intensity of 1,000 W/m^2 for 30 min. The distance from the lamp bottom to the membrane was fixed to about 225 mm. After the irradiation, two glass plates were carefully removed from the apparatus, and waters condensed on the plates were collected with a microsyringe to estimate the volumes. In this paper, waters obtained on the undersurface of the glass plate above and on the upper surface of the glass plate under the membrane are named as "evaporated water" and "permeated water," respectively (see Fig. 3b). When seawater was employed for the membrane permeation, the

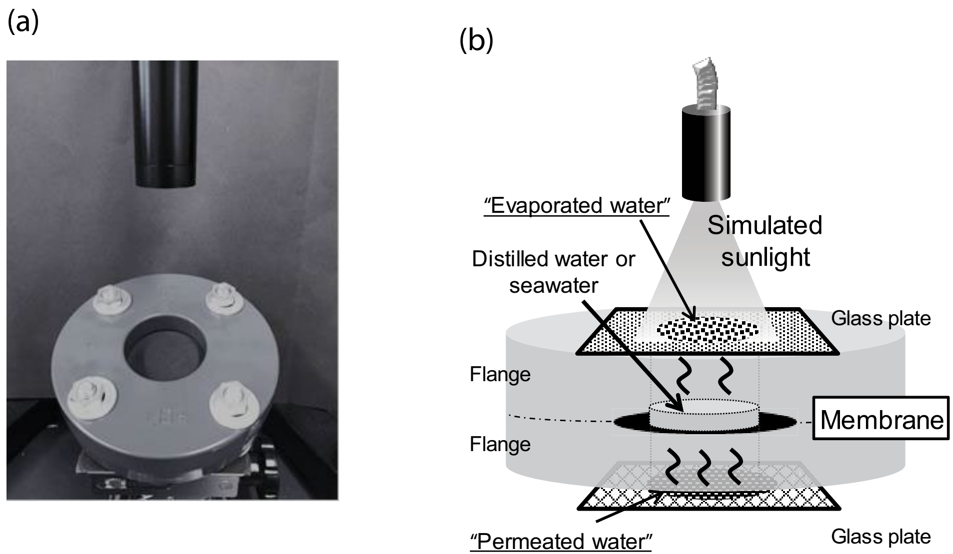

Fig. 3. (a) Image of the membrane permeation experiment using SB5 modified PTFE membrane sandwiched between two flanges (a slip-on type; in one flange, outer diameter: 115 mm, inner diameter: 42 mm, thickness: 14 mm). The distance from the lamp bottom to the membrane was about 225 mm. and (b) Schematic diagram of the membrane permeation experiment using flange system.

electric conductivities of the collected waters were measured by a conductance meter, B-771 LAQUAtwin compact conductivity meter (HORIBA, Ltd., Kyoto, Japan). From the electric conductivity, the salinity of the water was estimated [29]. In the experiments using seawater, all membranes were thoroughly washed with distilled water before use.

In the case of two-ply membrane system, a PTFE membrane (PTFE membrane filter; diameter: 90 mm) was directly sandwiched between two flanges and a cellulose membrane (diameter: 40 mm) was put on the PTFE membrane from the upper side of the combined flanges. The cellulose membrane was not sandwiched between the flanges. Water was slowly poured into the cylindrical space from the upper side of the system with removing air between the PTFE membrane and the cellulose one. The following procedures were the same as above mentioned.

2.4. Experiments of solar steam generation

Experiments of solar steam generation is carried out using a SB5 modified cellulose membrane (40 mm diameter). This membrane was put into a glass petri dish (inner diameter: 58 mm) and 3 mL of distilled water was poured into the dish slowly. After settling the membrane at the bottom, this set is put on an electric balance with an accuracy of 0.1 mg, and the simulated sunlight was irradiated (area: 50 × 50 mm) to the whole part of the membrane at the intensity of 1,000 W/m^2 for 30 min. The weight decrease of water by steam generation is measured with the balance [20–24]. After deducting the decrease of natural evaporation in dark place for 30 min, the actual weight loss by light irradiation was recorded.

2.5. Experiments of the desalination of actual seawater with natural sunlight

The desalination experiment of actual seawater using natural sunlight was performed at the roof terrace of building "I" of Tohoku center of National Institute of Advanced Industrial Science and Technology, northern latitude of about 38.3° and east longitude of about 140.9°. The solar energy was recorded with a solar power meter SPM-SD (SATO TECH., Kawasaki, Japan) beside the flange. The flange system was placed in a sunny spot for 4 h (~10 am to 2 pm) on a bright fine day of May. The weight difference of a petri dish (inner diameter: 58 mm; inner height: 17 mm) under the membrane between before and after the experiment was used for determining the volume of the permeated water. In this case, the petri dish was employed instead of the glass plate because a large volume of water was obtained under the membrane. The electric conductivities of the collected water were measured by a conductance meter, and the contents of Na, K, Ca, and NO_3 ion were analyzed by respective compact ion meters (LAQUAtwin; HORIBA, Ltd).

2.6. Ultraviolet-visible-near infrared spectrometry

Diffuse reflectance Ultraviolet-visible-near infrared (UV-vis-NIR) spectra of dye modified membranes were recorded by Shimadzu UV-3600 Plus spectrometer equipped with an integrating sphere. Kubelka Munk function was used for their diffuse reflectance spectra.

3. Results and discussion

3.1. Membrane permeation of water with SB5 modified PTFE membrane

In our previous papers about seawater desalination [28,29], two dyes, disperse red 1 (DR1) and disperse blue 14 (DB14), were employed. Recently we found a new dye, solvent black 5 (SB5), which is effective for water purification with artificial transpiration stream [34]. Then, the new dye SB5 was compared with dyes previously used. Fig. 4 shows the images of a DR1–DB14 doubly modified PTFE membrane (Fig. 4a) that was regarded as the best membrane in our previous paper [29] and an SB5 modified one (Fig. 4b). Both membranes are black in color to suggest their effective absorption of visible light. Fig. 5 illustrates diffuse reflectance UV-vis-NIR spectra of the DR1–DB14 doubly modified and the SB5 modified PTFE membrane. Solar irradiance spectrum at the surface of the earth (Air Mass 1.5: Global tilt W/m^2·nm) is overlaid. Although the doubly modified membrane absorbed the whole region of visible light, NIR (near infrared) light as a significant component of sunlight was scarcely used by this membrane. On the other hand, the spectrum of the SB5 modified PTFE membrane was well-overlapped with that of the solar irradiance from UV to NIR region. The SB5 modified membrane had the strongest absorption peak at about 500 nm in wavelength, where the highest intensity of solar irradiance is observed. This membrane considerably absorbed NIR light up to about 1,400 nm of wavelength. SB5 was less water-soluble than DR1 and DB14, and the use of a single dye was simpler to

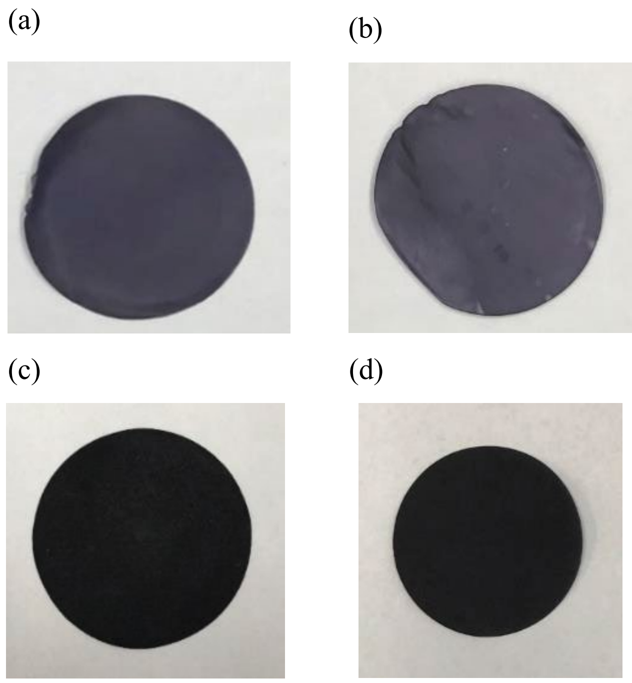

Fig. 4. Images of (a) DR1–DB14 doubly modified PTFE membrane (diameter: 47 mm), (b) SB5 modified PTFE membrane (diameter: 47 mm), (c) SB5 modified PTFE membrane (diameter: 55 mm), and (d) SB5 modified cellulose membrane (diameter: 40 mm). The scales of the images were adjusted.

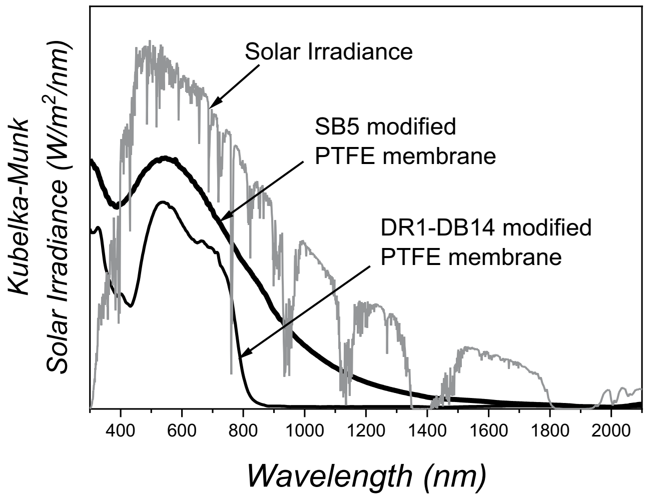

Fig. 5. Diffuse reflectance UV-vis-NIR spectra of DR1–DB14 doubly modified PTFE membrane and SB5 modified one (diameter: 47 mm). Kubelka-Munk functions are plotted against wavelength. Solar irradiance spectrum (Air Mass 1.5: Global tilt W/m^2/nm) is also overlaid with adjusted vertical scale.

prepare dye modified membrane. Thus, it is expected that the SB5 modified PTFE membrane is more efficient than other dye modified ones.

The comparison of the membrane permeation of distilled water through dye modified PTFE membranes were examined using an experimental system of petri dish we previously employed (Supplementary information S1), because this method is employed in our previous papers [27–29]. The results are summarized in Table 1. All PTFE membranes modified with dyes permitted the permeation of water under the irradiation of simulated sunlight at the intensity of 1,000 W/m^2 (1 SUN) for 30 min, while an original PTFE membrane without modification allowed no penetration of water. No water penetrations were observed in all membranes without light irradiation. The volume of the permeated water with a PTFE membrane doubly modified with DR1 and DB14 was higher than those with DR1 or DB14 modified membranes as previously reported [29]. However, the highest volume of the permeated water was found (51 × 10^{-3} mL), when an SB5 modified PTFE membrane was used. As expected from the spectrum of the SB5 modified PTFE membrane shown in Fig. 5, SB5 effectively absorbed nearly the whole wavelength range of the simulated sunlight including NIR light. SB5 generated more heat to promote membrane permeation. Thus, SB5 was ascertained to be the most effective dye modified to the PTFE membrane in the membrane permeation. Therefore, we used only SB5 modified membranes for subsequent experiments.

3.2. Improvement of membrane permeation process

In the experiments using the petri dish system, 0.5 mL of water was practically the maximum volume for putting on the membrane. Since the membrane was not tightly fixed in the apparatus, more than 0.5 mL of water often resulted in spilling from the membrane by its sagging. Then, we tightly fixed the SB5 modified PTFE membrane with two slip-on type

Table 1
Membrane permeation with PTFE membranes using petri dish system under the irradiation of simulated sunlight[a]

Dye modified to membrane	Volume of water (×10^{-3} mL)		
	Evaporated	Permeated	Total
Non	0	0	0
DR1	5	25	30
DB14	10	23	33
DR1–DB14	3	45	48
SB5	26	51	77
SB5[b]	21	47	68
SB5[b,c]	74	143	217

[a]Conditions: 0.5 mL of distilled water was put on PTFE membranes. Simulated sunlight was irradiated at the intensity of 1,000 W/m^2 for 30 min using a solar simulator (SAN-EI ELECTRIC Co. Ltd., XEF-300).
[b]Using flange system.
[c]3 mL of distilled water was used.

plastic flanges illustrated in Fig. 3. A larger PTFE membrane (PTFE filter paper PF050; diameter: 55 mm) was sandwiched between two flanges, and the flanges were tightened with four bolts as shown in Fig. 3a. An image of this SB5 modified PTFE membrane with a diameter of 55 mm is illustrated in Fig. 4c. As this membrane was thicker (0.36 mm thick) than the membrane 47 mm in diameter (0.075 mm thick), much more SB5 was modified on the membrane, which become blacker than the membrane with 47 mm diameter. The diffuse reflectance UV-vis-NIR spectrum of the membrane in the Supplementary information Fig. S2 indicated that the spectrum was analogous to that of the PTFE membrane (47 mm diameter) shown in Fig. 5. By using this flange system, more than 10 mL of water can be stably placed on the membrane. The results of the membrane permeation of distilled water using the flange system is also shown in Table 1. Even when 3 mL of distilled water was used, 143 × 10^{-3} mL of the permeated water (total volume including the evaporated water was 217 × 10^{-3} mL) was obtained without spilling of water on the membrane. As the experiment with 3 mL of water was impossible with the petri dish system, the employment of the flange system successfully increased the volume of water that can be treated at one time.

During the desalination process using a large volume of seawater, the volume on the membrane gradually decreases with time. Then, the effect of the water volume on the membrane permeation was examined using the flange system. As summarized in Table 2, the volumes of both the permeated and evaporated water were decreased with the water volume on the membrane, when the volume was more than 3 mL. In these cases, the energy of the irradiated light was significantly consumed for heating water on the membrane to suppress the vaporization of water. Hence, the volumes of the permeated and evaporated water were decreased. On the other hand, the volumes of the permeated and evaporated water using <3 mL of water were lower than that using 3 mL of water. In the flange system, 3 mL of water is the minimum volume for spreading all over the membrane in the cylindrical space (Fig. 6a). Water <3 mL formed a water

Table 2
Effect of water volume on the performance of membrane permeation[a]

Water volume (mL)	Volume of water ($\times10^{-3}$ mL)		
	Evaporated	Permeated	Total
0.5	21 (122)	47 (198)	68 (320)
1.0	24 (97)	30 (183)	54 (280)
2.0	40 (85)	52 (178)	92 (263)
3.0	74 (75)	143 (162)	217 (237)
5.0	64 (49)	121 (138)	185 (187)
8.0	46 (36)	87 (101)	133 (137)

[a]Conditions: Distilled water was placed on SB5 modified PTFE membrane (diameter: 55 mm). Simulated sunlight was irradiated at the intensity of 1,000 W/m^2 for 30 min using a solar simulator. In parentheses, the results using two-ply system (No. C) are listed.

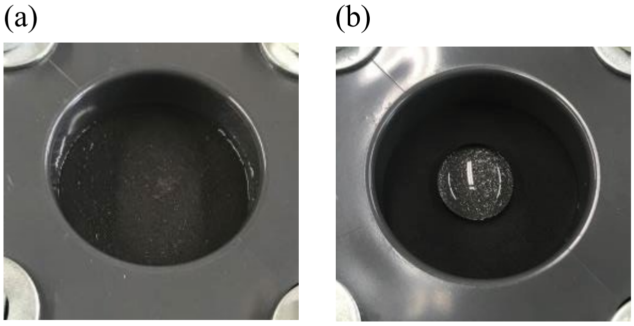

Fig. 6. States of distilled water on SB5 modified PTFE membrane. (a) 3 mL and (b) 1.0 mL.

drop on the PTFE membrane. For example, 1 mL of water became a small water drop on the membrane, which did not cover the whole membrane as shown in Fig. 6b. The decrease of the contact area of water with the membrane by the water drop formation caused the lower permeation of water. In the practical apparatus of this process, the formation of the water drops on the hydrophobic membrane is inevitable because the volume of seawater on the membrane is reduced with processing time. Although the employment of the hydrophobic membrane that prevents the penetration of liquid water and permits the permeation of gaseous water vapor is essential in our seawater desalination, the formation of the water drop on the membrane should be overcome.

3.3. Comparison of membrane permeation with solar still

As mentioned in the introduction, solar still is a well-known and simple water treatment by direct use of sunlight [12–15]. Even when photothermal materials are utilized [16–26], the condensation treatment of water vapor using solar still like apparatus is required for its recovery. The evaporated water recovered on the undersurface of the transparent plate above the membrane (evaporated water) was also obtained by the same mechanism as a solar still. Then, the comparison of our membrane permeation and solar still was examined. In the case of a solar still type experiment, a PMMA (polymethylmethacrylate) plate (50 mm square, 2 mm thickness) was sandwiched between the two flanges directly under the SB5 modified PTFE membrane. The membrane permeation is prevented by underlaying the PMMA plate and the vaporized water only diffuses upward. When 3 mL of distilled water was loaded into the cylindrical space with the solar still apparatus and the simulated sunlight was irradiated for 30 min, the volume of evaporated water was increased to 92 × 10^{-3} mL. However, this water volume was lower than that of the permeated water in the membrane permeation (143 × 10^{-3} mL). While the whole water must be warmed for vaporization in solar still, only the heating of water nearby the membrane is required in the membrane permeation because vaporized water near the membrane with dye quickly penetrates through the membrane. Thus, the superiority of seawater desalination by the membrane permeation to solar still was experimentally ascertained.

3.4. Two-ply system for membrane permeation process

As shown in Fig. 6b, the formation of water drop on the membrane is an inevitable problem in the membrane permeation. When a hydrophilic cellulose filter membrane was sandwiched in the flange system as a substitute for PTFE membrane, water readily spreaded to the membrane to drip down naturally. Using seawater, the dripped water was not desalinated. On the other hand, when a hydrophilic cellulose membrane was put on the PTFE membrane sandwiched in the flanges, 0.5 mL of water spread all over the cellulose membrane immediately, and no dripping of water under the PTFE membrane was found even when 10 mL of water was used. This observation provided an answer to overcome the formation of water drop on the PTFE membrane. Then, the membrane permeation was attempted by the combinations of two membranes, where a hydrophilic cellulose membrane was overlaid on a hydrophobic PTFE membrane. In this paper, this combination is called as "two-ply system." Then, four combinations of the two-ply system were attempted in the membrane permeation using the flange system. Table 3 summarizes the results of the four combinations of the two-ply system using 3 mL of distilled water (No. A, B, C, and D).

In the case of the two-ply system with non-modified cellulose membrane and PTFE membrane (No. A), modest volumes of water were permeated and evaporated. Since these membranes were slightly warmed by the light irradiation, a little volume of water was vaporized with these membranes. When non-modified cellulose membrane was put on the SB5 modified PTFE membrane (No. B), the volumes of both the permeated and evaporated water were increased (total volume: 152 × 10^{-3} mL) from the system No. A (total volume: 32 × 10^{-3} mL). However, these volumes were still lower than those with only SB5 modified PTFE membrane (total volume: 217 × 10^{-3} mL). On the other hand, the two-ply system where an SB5 modified cellulose membrane was placed on a non-modified PTFE membrane had the highest performance of the membrane permeation (No. C). The volumes of the permeated and evaporated water were 162 × 10^{-3} and 75 × 10^{-3} mL (total volume: 237 × 10^{-3} mL), respectively,

Table 3
Membrane permeation using two-ply system[a]

Two-ply membrane system			Volume of Water (×10^{-3} mL)		
No.	Cellulose (upper)[b]	PTFE (lower)[c]	Evaporated	Permeated	Total
A	Non	Non	11	21	32
B	Non	SB5	34	118	152
C	SB5	Non	75	162	237
D	SB5	SB5	70	165	235

[a]Conditions: 3 mL of distilled water was used. Simulated sunlight was irradiated at the intensity of 1,000 W/m^2 for 30 min.
[b]Diameter: 40 mm.
[c]Diameter: 90 mm.

which were higher than those using only SB5 modified PTFE membrane. As the cellulose membrane was more paintable than PTFE membrane with SB5, the SB5 modified cellulose membrane had a deep black in color as shown in Fig. 4d. The diffuse reflectance UV-vis-NIR spectrum of the SB5 modified cellulose membrane illustrated in Fig. 7 indicated that this membrane also harvested approximately the whole sunlight as well as the SB5 modified PTFE membranes. In this case, the simulated sunlight was absorbed by SB5 modified on the cellulose membrane to produce heat, which effectively vaporized water near the cellulose membrane. The vaporized water penetrated through the PTFE membrane attaching the cellulose membrane. In the case of the two-ply system where both membranes were modified with SB5 (No. D), the volumes of the permeated and evaporated water was approximately similar to those of the two-ply system No. C. No SB5 is required in PTFE membrane, when SB5 is modified to the cellulose membrane. Thus, the two-ply system No. C was the most effective combination for the membrane permeation.

Using the two-ply system No. C, the effect of water volume on the membrane permeation was examined again, and the results are also summarized in the parentheses of Table 2. In these cases, even small volumes of water <3 mL thinly spread all over the SB5 modified cellulose membrane. The volumes of the permeated and evaporated water monotonically increased with the decrease of the water volume on the membrane. In the case using 0.5 mL of distilled water, 198 × 10^{-3} mL of the permeated water and 122 × 10^{-3} mL of the evaporated water (totally 320 × 10^{-3} mL that was more than 60% of the water used) were produced. Even in the cases using more than 3 mL of distilled water, the volumes of the permeated water were higher than those with SB5 modified PTFE membrane. Thus, the two-ply membrane system consisting of SB5 modified cellulose membrane and non-modified PTFE membrane (No. C) was more effective than SB5 modified PTFE membrane in all water volumes. When this process is put into practical applications, SB5 modified membrane will be replaced constantly by its gradual deterioration with the continuous exposure to sunlight. In the two-ply membrane system No. C, while the SB5 modified cellulose membrane will be exchanged regularly, the non-modified PTFE membrane can be used for a longer time than the SB modified cellulose membrane, because the PTFE membrane was not directly exposed to sunlight.

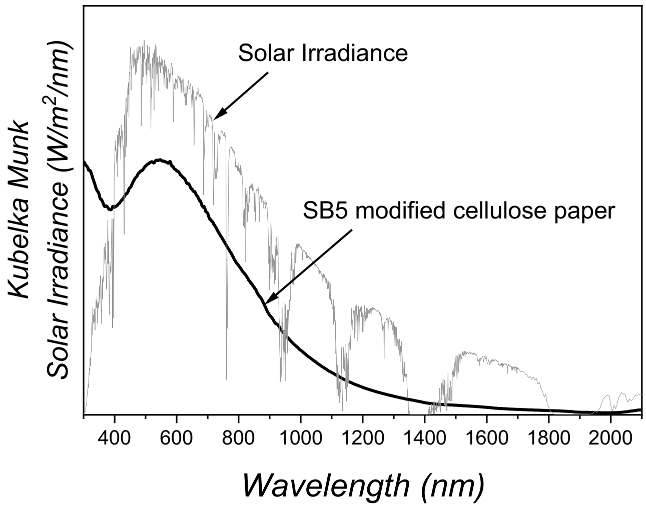

Fig. 7. Diffuse reflectance UV-vis-NIR spectrum of SB5 modified cellulose membrane (Kubelka-Munk function is plotted against wavelength). Solar irradiance spectrum is also overlaid with adjusted vertical scale.

Since the cellulose membrane is considerably less expensive than PTFE membrane, the two-ply system No. C is more effective than that using only SB5 modified PTFE membrane even from the aspect of cost.

3.5. Solar desalination of artificial seawater using two-ply system

The membrane permeation of seawater was next examined using the two-ply system No. C for solar desalination of seawater. In these experiments, artificial seawater (MARINE ART SF-1) was used. As summarized in Table 4, the two-ply system No. C was a powerful system of solar desalination of seawater. In the case using 3 mL of the artificial seawater, 147 × 10^{-3} mL of the permeated water was obtained under the membrane. The salinities of all recovered permeated waters estimated from their electric conductivities were <0.01%. As the salinity of freshwater is <0.05%, the artificial seawater was efficiently desalinated to freshwater by the membrane permeation using simulated sunlight. As mentioned above, for the production of 1.5 L of drinkable freshwater, more than 1.5 L of seawater must be loaded on the membrane.

Table 4
Seawater desalination using two-ply system under irradiation of simulated sunlight[a]

Seawater volume	Volume of water ($\times 10^{-3}$ mL)			Electric conductivity[b] (μS/cm)
	Evaporated	Permeated	Total	
0.5	105	187	292	12 (<0.01)
3.0	75	147	223	10 (<0.01)
3.0[c]	78	131	208	52 (<0.01)

[a]Conditions: Artificial seawater (MARINE ART SF-1) was used. Simulated sunlight was irradiated at the intensity of 1,000 W/m² for 30 min.
[b]Salinity in parentheses.
[c]Saturated artificial seawater was used.

During the desalination treatment, seawater on the membrane becomes concentrated gradually with the production of desalinated water, and finally, the seawater will be saturated. RO process cannot desalinate concentrated seawater with more than 7% salinity [5]. Then, the desalination of saturated seawater was attempted using the two-ply system. When 3 mL of saturated seawater (~26% salinity) was used, 131×10^{-3} mL of the permeated water was produced, whose salinity was also <0.01% (Table 4). The effective desalination of the saturated seawater indicated that this process applies to the desalination of concentrated and saturated seawater. This is beneficial in practical seawater desalination because the environmentally friendly disposal of concentrated seawater after desalination is also an important problem of freshwater production [5,36].

The energy efficiency of the freshwater production from the artificial seawater was estimated using the following calculation:

$$\eta(\%) = \frac{H_v}{Q_e} \times 100$$

where η is energy efficiency, H_v is the vaporization heat of recovered water, and Q_e is the energy of the irradiated simulated sunlight to the cylindrical space of the flange. In this equation, the energies consumed for heating water, membranes and flanges, and the vaporization heat of unrecovered water vapor are not included. Details of this calculation are described in the Supplementary information S2. In the case using 3 mL of the artificial seawater, the energy efficiency for the production of the permeated water as recovered desalinated freshwater (147×10^{-3} mL) was about 14.5%. The total efficiency for the permeated and evaporated water (223×10^{-3} mL) was calculated to 22.0%. Productivities of freshwater are evaluated to 234 g/m² h (permeated water) and 355 g/m² h (total volume of evaporated and permeated water) using sunlight (1,000 W/m²). Although these energy efficiencies were lower than those of our previous paper using the petri dish apparatus [29], the decreased efficiencies seem to result from the upsizing of the irradiated area using the flange system. The irradiation area of the simulated sunlight in our previous paper (113 mm²) was less than one-tenth of that in this study (1,385 mm²). Importantly, while only 47×10^{-3} mL of desalinated water was obtained in our previous case [29], more than 200×10^{-3} mL of desalinated water was produced by the flange apparatus with the two-ply system.

3.6. Comparison with solar steam generation

Photothermal materials and water steam generation using them are rapidly advanced recently, and the energy efficiencies in these researches are generally high [20–26]. On the other hand, water vapor generated with those materials by simulated sunlight is not recovered and the energy efficiencies are calculated with the weight decrease of water in most cases [20–24]. Hence, these estimations are different from the productivity of recovered freshwater. Then, the SB5 modified cellulose membrane was put in a petri dish with 3 mL of distilled water and was exposed to the simulated sunlight for 30 min. The weight loss after 30 min irradiation was ~0.320 g. This value was considerably higher than the total volumes of the evaporated and permeated water listed in Table 2 (237×10^{-3} mL). It is thought that much more volume of water than the recovered volume was converted to water vapor using the SB5 modified cellulose membrane. On the other hand, when the glass plate above the membrane was removed, the volume of the permeated water decreased from 162×10^{-3} to 116×10^{-3} mL. These observations suggested that the performance of the membrane permeation is greatly different from the solar steam generation, and the freshwater production was significantly affected by the desalination apparatus. Therefore, the simple comparison of our membrane permeation with the solar stream generation is not accurate.

3.7. Desalination of actual seawater using natural sunlight

The desalination of actual seawater using natural sunlight was finally attempted, where actual seawater collected at Sanriku seacoast and natural sunlight at the roof terrace of a building of our institute were applied. The two-ply system (No. C) with 5 mL of the actual seawater was located in a sunny area for 4 h (about 10 am to 2 pm of Japan time) on a sunny day. The total energy of sunlight for 4 h monitored at the same place was ~11×10^6 J/m², and the average of the solar energy per second was about 770 W/m². In a Supplementary information Fig. S3, the monitored solar energy was illustrated. In a glass petri dish under the membrane, ~3.0 g of water was recovered after 4 h. The measured electric conductivity of the permeated water was 6 μS/cm to indicate that this recovered water was effectively desalinated. As summarized in Table 5, some representative ions of the natural seawater were perfectly removed in the permeated water. Thus, ~60% of actual seawater was efficiently desalinated to freshwater

Table 5
Comparison of quality of waters

Item	Actual seawater	Permeated water
Electric conductivity (μS/cm)	>20 × 10³ [a]	6
Na ion content (mg/L)	>9,900[a]	<2[b]
K ion content (mg/L)	380	<2[b]
Ca ion content (mg/L)	350	<1[b]
NO_3 ion content (mg/L)	950	<6[b]

[a]Over measurement range.
[b]Under measurement range.

by the direct use of natural sunlight. The water productivity of the water collected in the petri dish under the membrane was 597 g/m² h, and the energy efficiency was 48.1%. These results demonstrated that the two-ply system was also active for the actual solar desalination of seawater.

3.8. Evaluation of freshwater production from seawater

As listed in Table 4, by the irradiation of simulated sunlight (1,000 W/m² intensity) for 30 min, 147×10^{-3} mL of desalinated freshwater was produced from 3 mL of seawater as the permeated water, which was easily collected from the lower side of the apparatus (see Fig. 1). When this solar insolation continues for 6 h in a day (for example, in desert area), about 1.76 mL of fresh water can be produced from 3 mL of seawater. As the daily requirement of drinking water for one adult is assumed to 1.5 L [33], ~1.18 m² of the membrane area is required for producing the drinkable fresh water from seawater by the two-ply system (Supplementary information S3). Using the result of the desalination of actual seawater using natural sunlight for 4 h, the required membrane area for the production of 1.5 L of freshwater is calculated to be only 0.64 m². These estimated areas are considered to be practical for the production of drinking water for one person. The seawater desalination by our membrane permeation requires no facilities other than seawater and sunlight. More importantly, this process is an environmentally-friendly freshwater production, because it consumes no fossil fuels [4].

4. Conclusions

This paper reports our latest approaches to the improvement of seawater desalination with solar energy using dye modified membranes toward practical freshwater production. At first, solvent black 5 (SB5) was applied as a new dye modified to membranes. A PTFE membrane modified with SB5 that absorbs a wide range of sunlight including NIR light had better performances of the membrane permeation than DR1–DB14 doubly modified PTFE membrane previously reported [29]. Using the experiment apparatus with two flanges, the improvement of the membrane permeation was successfully achieved, where more than 1 mL of water can be loaded onto the SB5 modified PTFE membrane sandwiched between two flanges. When hydrophilic cellulose membrane was put on hydrophobic PTFE membrane for forming two-ply system, water readily spread throughout the inside of the flanges. The two-ply system with SB5 modified cellulose membrane and non-modified PTFE one was an effective combination. Artificial seawater was efficiently desalinated to produce freshwater using the two-ply system by the irradiation of simulated sunlight. Approximately 3 mL of freshwater was produced from actual seawater using natural sunlight for 4 h with this two-ply system. These results made substantial progress in seawater desalination by the direct use of solar energy toward large scale production of freshwater.

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Supplementary information

S1. Experiment of membrane permeation of water with petri dish system

The experiment of the membrane permeation of water with petri dish system was basically carried out with the same apparatus used in our previous papers [27–29]. Typical procedures are as follows. A PTFE membrane (PTFE membrane filter; diameter: 47 mm) was put on a Teflon holding ring platform (outer diameter: 37 mm, inner diameter: 33 mm, thickness: 3 mm) in a borosilicate glass petri dish. A glass plate (made of borosilicate glass) was overlaid for covering the petri dish. On all PTFE membranes, 0.5 mL of distilled water did not spread to form a water drop, whose contact area with the membrane was ~113 mm^2 (about 12 mm in diameter). In this study, an O-ring made of PTFE was put on the membrane for avoiding the spilling of the water.

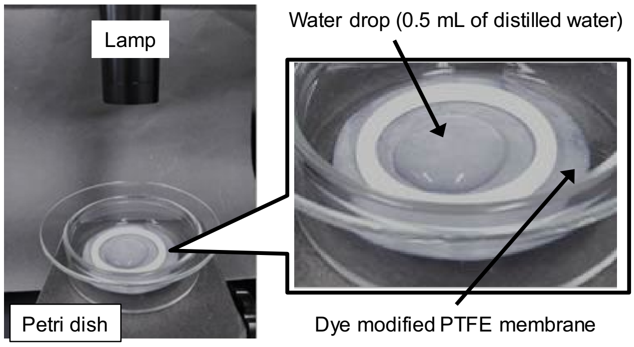

Fig. S1. Experimental apparatus of the membrane permeation by petri dish system.

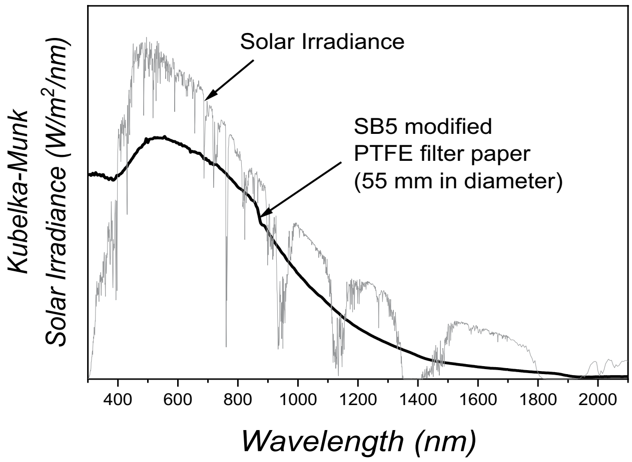

Fig. S2. Diffuse reflectance UV-vis-NIR spectrum of a SB5 modified PTFE membrane prepared from PTFE filter paper (diameter: 55 mm).

S2. Calculation of energy efficiency

The efficiency of the energy conversion from the simulated sunlight to the production of desalinated freshwater was simply calculated from the volumes of the permeated and evaporated water using the vaporization heat of water (2,461 J/g). Supplied energy was estimated from the intensity of irradiated sunlight (1,000 W/m^2 = 1,000 J/s/m^2) and irradiated area (ϕ42; 21 × 21 × 3.14 ≈ 1,385 mm^2 = 1,385 × 10^{-6} m^2) and irradiation time (30 min; 60 sec × 30 = 1,800 sec).

For example, in the case of 3 mL of seawater, 147 × 10^{-3} mL (147 × 10^{-3} g using specific gravity = 1) of the permeated water in Table 4;

Energy efficiency (only the permeated water; 147 × 10^{-3} g) = [(147 × 10^{-3} g) × (2,461 J/g)]/[(1,000 J/sec/m^2) × (1,800 s) × (1,385 × 10^{-6} m^2)] ≈ 14.5%.

Total energy efficiency (the permeated and evaporated waters; 223 × 10^{-3} g) = [(223 × 10^{-3} g) × (2,461 J/g)]/[(1,000 J/sec/m^2) × (1,800 s) × (1,385 × 10^{-6} m^2)] ≈ 22.0%.

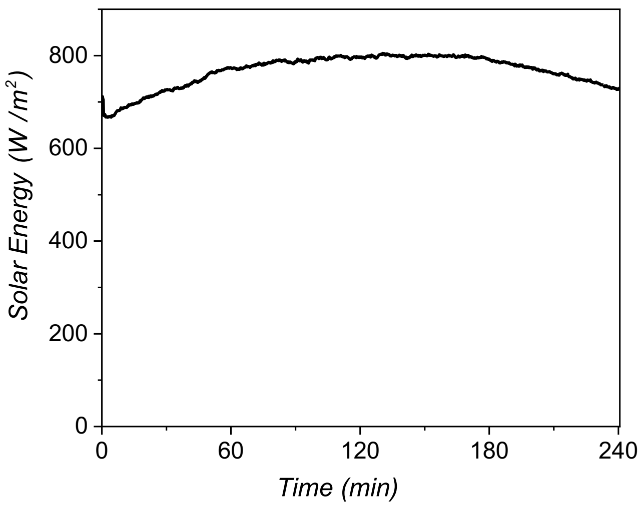

Fig. S3. Monitored solar energy in desalination of actual seawater using natural sunlight.

S3. Calculation of required land area for producing freshwater for one person

The required land area of solar irradiation for producing freshwater for one person is simply calculated by the volumes of the permeated water with the result of Table 4 with 3 mL of seawater.

30 min irradiation at the intensity of 1,000 W/m^2; 147 × 10^{-3} mL of freshwater production.

When solar insolation for 6 h at the intensity of 1,000 W/m^2 is obtained assuming the conduction in desert area: 1,764 × 10^{-3} mL of freshwater production.

The irradiated area of Table 5: ϕ42; 21 × 21 × 3.14 ≈ 1,385 mm^2 = 1,385 × 10^{-6} m^2.

Daily requirement of drinking water for one adult: 1.5 L [33].

Required land area for producing freshwater for one person = (1.5 L) × (1,385 × 10^{-6} m^2)/(1,764 × 10^{-3} mL) ≈ 1.18 m^2.