Water desalination using visible light by disperse red 1 modified PTFE membrane

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HIGHLIGHTS

- Water permeated through DR1 modified PTFE membrane by visible light irradiation.
- Water penetration through the membrane took place with photo isomerization of DR1.
- Desalination of NaCl solution was achieved by the light induced membrane permeation.
- Simulated solar light from solar simulator was effective for the water desalination.

GRAPHICAL ABSTRACT
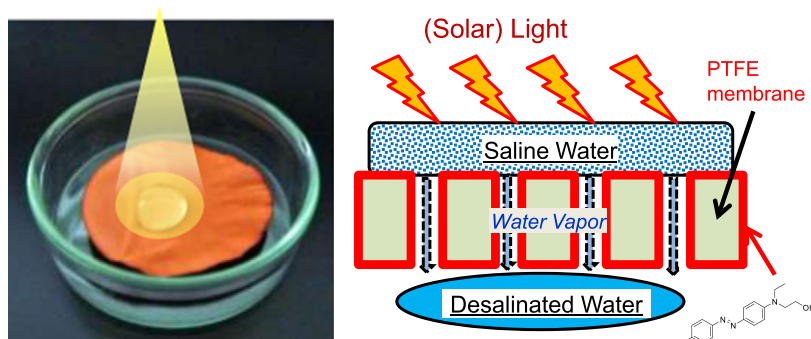
ARTICLE INFO

ABSTRACT

Water purification and seawater desalination are current desired technologies because global water shortage becomes more serious. As this problem is related to global warming, the energy for the processes should be covered by renewable energies like solar light. It was found recently that water droplets on azobenzene modified anodized alumina membranes permeate the membrane under light irradiation to be purified and desalinated. This paper reports an advanced system of the light induced water treatment, where disperse red 1 (DR1) modified PTFE (polytetrafluoroethylene) membranes are employed. Hydrophobic PTFE membrane inhibits the natural infiltration of raw water into the membrane to prevent the contamination of treated water. Disperse red 1 photoisomerizes only with visible light to adopt to the utilization of solar light. Waters on the DR1 modified PTFE membrane penetrated the membrane under visible light irradiation. 3.5% NaCl solution was desalinated to purified water (<0.01% NaCl) by the membrane permeation process. A simulated solar light of a solar simulator was very effective for this desalination to produce clarified water from an artificial seawater. These results indicate that solar desalination is realizable with the DR1 modified PTFE membrane by the direct irradiation of solar light to the membrane.

1. Introduction

Water purification and seawater desalination are now globally important technologies. As the shortage of fresh water is involved with global warming (climate change) by the consumption of fossil fuels and the resulting carbon dioxide emission, renewable energies,

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especially solar light, free from fossil fuels should be employed for these water treatments [1–4]. Recently, the energy of light is actively applied to water purification processes using light-to-heat conversion materials, which promote the steam generation by water evaporation under light irradiation [5–11]. For example, Au plasmonic nanoparticle enables localized heating and efficient water evaporation [6]. Titanium nitride nanoparticles as a lossy plasmonic nano-resonator are reported to be more active than gold nanoparticles for light induced steam generation [7]. Carbon materials based fluids are also claimed to be effective for the direct vapor generation with solar light [8]. As the steams thus formed by water evaporation must be recovered from the plate located above water pools containing these heating materials, the corresponding water purification apparatuses are essentially regarded as variations of solar still system, which generally requires complicated equipments to collect vaporized and condensed water [12,13]. The purified water condensed on the undersurface of transparent plate above raw water must be recovered carefully without its dripping into the raw water. This complicated operation is thought to prohibit the progress of the solar still. Membrane materials are also studied for the heat generation under light irradiation. For example, photo thermal membranes based on poly-pyrrole coated stainless steel mesh [9] and three layered membranes consisting TiO_2 nanoparticles, Au nanoparticles and anodized aluminum oxides [10] are studied for vapor generation. Double-layer structure consisting of a carbon foam layer supporting an exfoliated graphite layer is active for vapor generation as well [11]. However, even in these cases, no water vapors produced by the heating processes penetrate the membranes, and the recovery manners of the treated waters are essentially similar to the solar still [1–4,12,13]. Therefore, simpler systems of purified water production, especially in the recovery of the treated water, are desired for the practical water treatments with light energy.

The application of azobenzene modified materials to control mass transport and diffusion under light irradiation are previously reported [14,15]. For example, the release of cholesterol from an azobenzene-tethered mesoporous silica powder is promoted by the simultaneous irradiation of UV and visible lights [14]. The flow rate of organic solvents through an azobenzene modified silica gel column can be accelerated by the same simultaneous light irradiation [15]. The UV and visible lights isomerize the azobenzene molecules from trans to cis isomer and from cis to trans isomer, respectively. The simultaneous irradiation of these two lights induces the repetitive photo isomerization of the azobenzene between the trans and cis isomer in the small spaces of silica pores, activating the movement of nearby molecules to enhance their transfer. Although the molecular motions of azobenzene derivatives are well utilized for some intelligent and functional materials [16–18], the applications of these repetitive photo isomerizations are not so often reported [19–21]. Recently, azobenzene modified anodized alumina membranes were employed for a light promoted mass transfer [22]. When a water droplet on the azobenzene modified membrane was exposed to UV and visible lights, a certain volume of the water was recovered under the membrane by membrane penetration, while no water permeation occurred without the UV and visible lights irradiation. It is thought that the repetitive photo isomerization of azobenzene elicited by the simultaneous irradiation provokes the evaporation of the water to result in the membrane permeation of water. When the solutions of rhodamine B and NaCl were used in the light induced membrane permeation, the penetrated waters were purified or desalinated. No rhodamine B was contained in the treated water and the salt water was converted into fresh water. From these results, an installation of seawater desalination using the azobenzene modified membrane under solar light irradiation was proposed in the paper [22]. Fig. 1 illustrates the concept of this system that seawater in a pool on an azobenzene modified membrane is exposed to solar light to produce purified desalinated water under the membrane, which is readily collected in the container under the membrane. In this system, the energy for seawater desalination is provided from solar light.
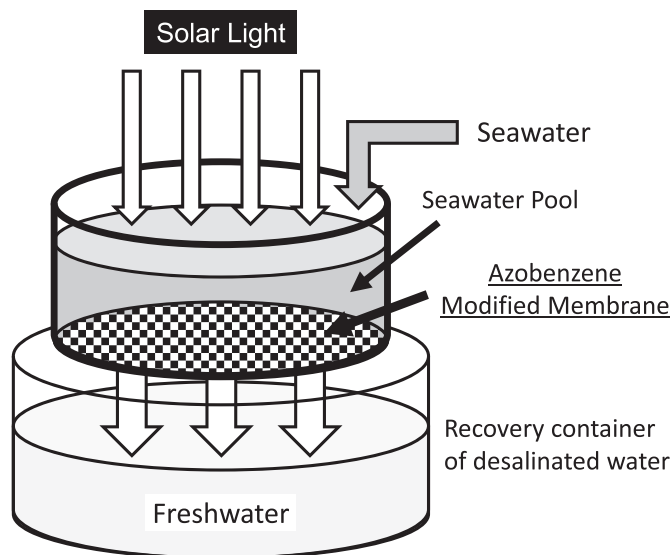

Fig. 1. A proposed membrane seawater desalination equipment using solar light energy.

In the system of Fig. 1, the natural dropping-down of seawater through the membrane must be avoided for preventing the contamination of the desalinated water under the membrane. In this point, the anodized alumina membrane is not suitable because of its hydrophilic and fragile property. The hydrophilicity facilitates the natural dropping-down of raw water and the fragility is unfavorable in large scale systems. On the other hand, 4-phenylazophenol mainly employed as the azobenzene compound in the previous paper [22] is inappropriate in the system of Fig. 1 using solar light, because its photo isomerization from trans to cis isomer requires UV light with wavelength of 350 nm that is scarcely contained in solar light. Then, this paper reports an improved light induced water treatment process, where PTFE (polytetrafluoroethylene) membrane that is highly hydrophobic and more robust than the anodized alumina membrane and disperse red 1 (DR1) that photo-isomerizes only with visible light of wavelength from 420 to 550 nm (Fig. 2) [23–27] were employed as alternative membrane and azobenzene compound, respectively. DR1 is known as a water-insoluble azobenzene dye, which is profitable for preventing the contamination of treated water with DR1. This paper also presents the desalination of 3.5% NaCl solution and an artificial seawater using the DR1 modified PTFE membrane under a simulated solar light, which is an important step toward the direct solar desalination using the system shown in Fig. 1.

2. Experimental section

2.1. Materials

Polytetrafluoroethylene (PTFE) membranes used in this study were Advantec PTFE membrane filters from Toyo Roshi Kaisha, 47 mm in diameter and 0.8 μm or 3.0 μm of pore size. Polyethersulfone (PES) membrane was PES membrane filter of As One Corporation (47 mm in diameter). Disperse red 1 [N-ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline] (Fig. 2) was purchased from Sigma-Aldrich Co. LLC. MARINE ART SF-1 for artificial seawater [28] was bought from Osaka Yakken Co., Ltd. Other organic reagents and NaCl (special grade) were obtained from Wako Pure Chemical Industries, Ltd.

2.2. Preparation of disperse red 1 modified membranes

After wetting a sheet of PTFE membrane filter with isopropanol, 2 mL of 0.1 g/mL solution of disperse red 1 (DR1) in DMF (N,N-dimethylformamide) was embraced to the membrane filter in a
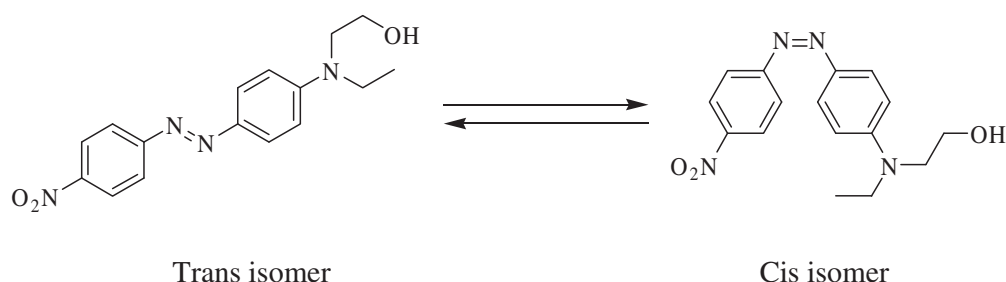
Trans isomer   Cis isomer

Fig. 2. Photo isomerization of disperse red 1 (DR1).

Teflon vessel. After 3 days, the membrane was taken from the vessel and heated at 40 °C for 1 day in air. This membrane was immersed in 50 mL of distilled water for 1 day. This washing treatment was repeated until the concentration of DR1 in the washing water decreased to <1 ppb monitored by spectrometer analysis (using JASCO V-530 spectrometer). The concentration of DR1 in the first washing water was <1 ppb in nearly every cases. The membrane thus treated was finally dried at 40 °C for 1 day. DR1 modified PTFE membranes using the membranes with 0.8 or 3.0 μm of pore size were named as **Memb-1** and **Memb-2**, respectively. DR1 modified PTFE membrane using 1 mL of a diluted DR1 solution (0.05 g/mL) was named as **Memb-3**. Double modified membrane (**Memb-4**) was obtained from a single modified PTFE membrane (one **Memb-1** membrane) by the direct recoating with 0.5 mL solution of DR1 in DMF (0.1 g/mL) for 4 day. The following treatment was the same as above. DR1 modified PES membrane (**Memb-5**) was prepared by the immersion of a PES membrane in 2 mL of 0.1 g/mL isopropanol solution of DR1, because the PES membrane is soluble in DMF. Other procedures were the same as the DR1 modified PTFE membrane.

2.3. Procedures of membrane permeation of distilled water

The experiments of water permeation through membranes were performed with the apparatus system shown in Fig. 3. The membrane (47 mm in diameter) on a Teflon holding ring platform (37 mm in external diameter, 33 mm in internal diameter and 3 mm thick) was put into a glass petri dish. On the nearly central part of the membrane, 0.5 mL of distilled water was dropped slowly (Fig. 4). The contact area of the droplet with the membrane was approximately 1.1 cm^2 (roughly a circle of diameter 1.2 cm). In all tests using PTFE membranes, the contact areas of 0.5 mL of water were the same. A watch glass was overlaid on the petri dish. This watch glass transmits visible light, but filters out UV light. This apparatus system was placed in a dark space for obscuring room light. In all experiments, the system was not cooled purposefully.
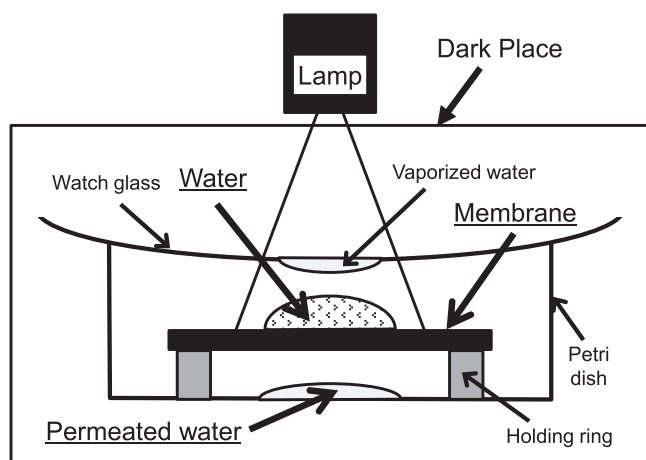
Visible light irradiation was carried out using a xenon light source MAX-301 (300 W xenon lamp; Asahi Spectra Co. Ltd.) equipped with a VIS mirror module (Asahi Spectra Co. Ltd.), which controls the irradiated light mainly in the range of from 385 to 740 nm in wavelength. This mirror module efficiently eliminates near-infrared light from xenon lamp to be free from its heat effect. The distance between the lamp bottom and the membrane was fixed to approximately 30 mm in the case of the visible light irradiation. The light was irradiated to the whole water (see Graphical Abstract). The irradiation of a light with wavelength of 440 nm was achieved by using a corresponding bandpass filters. After the light irradiation, the temperature of the remained water on membrane was measured with a sharpened thermocouple promptly, and the water was removed with a syringe to determine the volume by its scale. After picking up the membrane, the volumes of water on the bottom of the petri dish under the membrane and of water on the undersurface of the watch glass above the membrane were estimated with suitable microsyringes for HPLC, which could collect the water effectively by their flat needle tip. When a solar simulator (Fiber Solar Simulator XEF-300, SAN-EI ELECTRIC CO., LTD.) was used, the light intensity at the surface of the membrane was fixed at 1 SUN, where the distance between the lamp bottom and the membrane was approximately 220 mm. Other procedures were the same as the case of the xenon light source. On the other hand, 0.5 mL of water put on DR1 modified PES membrane did not form a droplet to be seeped into the whole membrane.

2.4. Procedures of desalination of NaCl solution and artificial seawater

In the desalination experiment of NaCl solution, 3.5% NaCl solution prepared from NaCl and ultrapure water was used. An artificial seawater was obtained from MARINE ART SF-1 [28] and ultrapure water. The light induced water permeation was performed by the same

Fig. 3. Schematic diagram of the experimental apparatus of water membrane permeation.

Fig. 4. A droplet of distilled water (0.5 mL) on a DR1 modified PTFE membrane.

manner as the case of distilled water. After measuring the volume of permeated water under the membrane, the electric conductivity of the water and the corresponding NaCl concentration were analyzed by a conductance meter, B-771 LAQUAtwin compact conductivity meter (HORIBA, Ltd). As the volumes of the permeated water were insufficient for the conductivity meter (minimum volume: approximately 120 μL), additional water (100–150 μL of distilled water; electric conductivity: 1–3 μS/cm) was mixed to the permeated water. After measuring the electric conductivity of the mixed water, the corrected electric conductivity of the permeated water was calculated by multiplying the electric conductivity by the reciprocal number of the dilution ratio. As the electric conductivity (and NaCl concentration) in the additional distilled water was not considered in this correction, the true value of the electric conductivity of the permeated water must be less than the value thus calculated. In the repeated experiments, NaCl solution on the membrane was replaced by fresh NaCl solution in each run. However, the membrane was not washed before the following experiment, because the washing of the membrane after each experiment that removes NaCl in the membrane is not suitable for evaluating the influence of NaCl fouling on the reproducibility of desalination. The repeated experiment with the artificial seawater was performed in the same manner as the NaCl solution.

2.5. Sample characterization

The absorption spectra of solutions were analyzed by JASCO V-530 spectrometer. The diffuse reflectance UV–vis spectra of the membranes were recorded with JASCO V-550 spectrophotometer equipped with an integrating sphere. Kubelka-Munk function was used to indicate the diffuse reflectance spectra of membranes. The images of scanning electron microscope (SEM) were obtained by JSM-6390 (JEOL).

3. Results and discussion

3.1. Preparation of disperse red 1 modified PTFE membranes

At first, the natural dropping-down of water through PTFE membrane was tested using the experiment apparatus shown in Fig. 3. After 0.5 mL of distilled water was put on a non-modified PTFE membrane for 1 h in a dark place, no water was found under the membrane and the whole volume of the water was remained on the membrane. Even after 5 h, nearly whole volume of the water was recovered on

the membrane. Thus, no natural permeation of water through the PTFE membrane was confirmed. In the previous research [22], azobenzene derivatives are tethered onto the surface of anodized alumina membrane using a silane coupling reagent, because the alumina surface is applicable to the surface grafting process with the silane reagent. However, as the surface of PTFE is unsuitable for this surface modification, a simple embrocation of DMF solutions of DR1 onto PTFE membrane was applied. The images of some membranes are shown in Fig. 5. The white original PTFE membrane (Fig. 5A) colored to dark red by the modification of DR1 (Fig. 5B; **Memb-1**). When this DR1 modified membrane was immersed in acetone, DR1 was gradually eliminated from the membrane. It is thought that the binding mode between DR1 and PTFE is simple absorption. However, the elution of DR1 into water was negligible in soaking test in distilled water according to the visible spectra of the treated water solution. The DR1 modified membrane using a diluted solution (**Memb-3**) had a lighter red color than the membrane **Memb-1**. Fig. 6 compares the spectra of solar light (line A) and DR1. The spectrum of DR1 acetonitrile solution (line B) had the peak absorption around 500 nm in wavelength, which isomerizes DR1 from trans to cis isomer. The photo isomerization from cis to trans isomer occurs under visible light irradiation with wavelength of longer than 530 nm [27]. As this visible light is the strongest component of solar light, DR1 is expected to absorb the solar light with high efficiency. In the diffuse reflectance spectrum of DR1 modified PTFE membrane (**Memb-1**) in Kubelka-Munk function (line C), the absorption peak of the membrane was shifted to shorter wavelength (approximately 440 nm). As the wavelength of the absorption peak of DR1 solutions is significantly affected by the solvents used [27], it seems that the interaction of DR1 with PTFE resulted in this blue shift. However, the photo isomerization of DR1 from trans to cis isomer is possible only by visible light even in the PTFE membrane. On the other hand, DR1 modified PES membrane (**Memb-5**) is in clear light red color (Fig. 5E), which had the absorption peak at approximately the same wavelength as the DR1 solution (line D of Fig. 6).

To the membrane **Memb-1**, visible light with wavelength of 440 nm was irradiated for observing the photo isomerization of DR1 on PTFE membrane. The diffuse reflectance UV–vis spectra of the membrane are shown in Fig. 7. The absorption around 440 nm in wavelength gradually decreased with the irradiation time (Fig. 7A). Thus, the photo isomerization of DR1 on the surface of PTFE membrane from trans to cis isomer by the light irradiation was ascertained. When visible light with wavelength ranging from 385 to 740 nm was irradiated to the
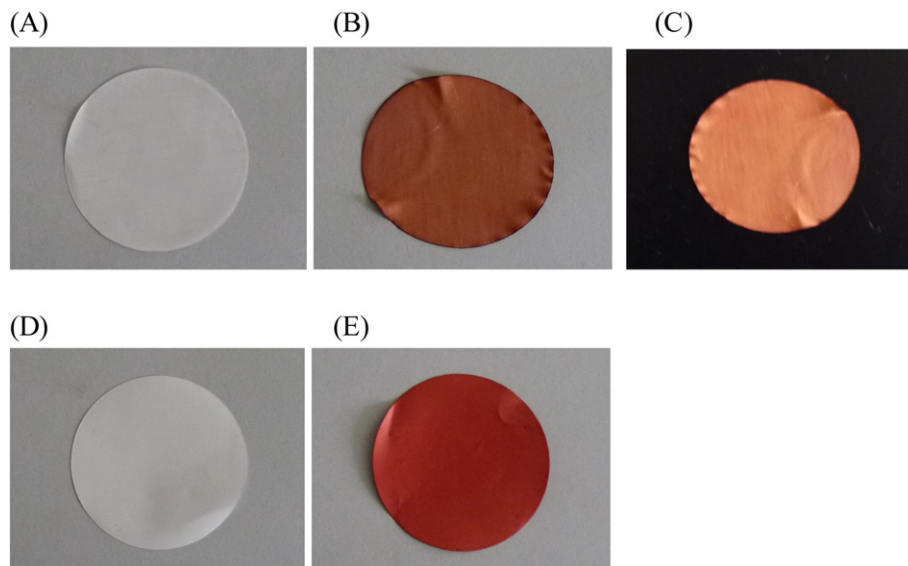
Fig. 5. (A) Original PTFE membrane, (B) DR1 modified PTFE membrane (pore size: 0.8 μm: **Memb-1**), (C) DR1 modified PTFE membrane with diluted solution (**Memb-3**), (D) Original PES membrane, and (E) DR1 modified PES membrane (**Memb-5**).
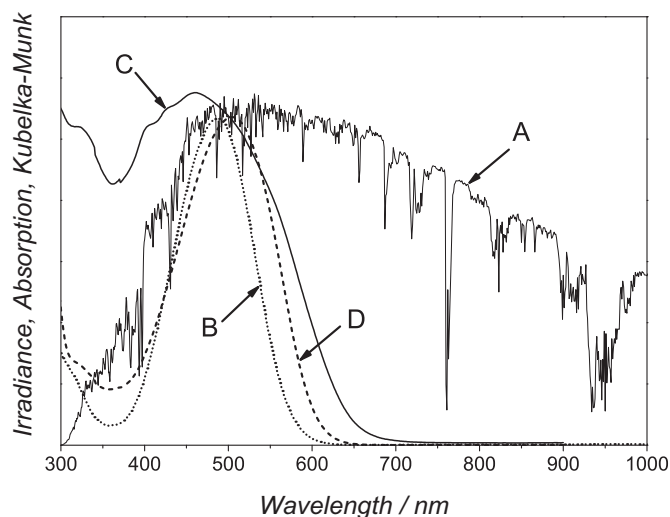
Fig. 6. (A) Spectra of solar light (Irradiance), (B) DR1 in acetonitrile (Absorption), (C) diffuse reflectance spectrum of DR1 modified PTFE membrane (**Memb-1**; Kubelka-Munk), and (D) diffuse reflectance spectrum of DR1 modified PES membrane (**Memb-5**; Kubelka-Munk). The values of Y-axis are adjusted.

membrane for 10 min, the decrease of the absorption around 440 nm was the same as the irradiation of 440 nm for 60 min (Fig. 7B). The light with a wider range of wavelength promoted the photo isomerization much more than that only of 440 nm. The longer irradiation of the visible light for 60 min decreased the absorption moderately. It is thought that the photo isomerization between trans and cis isomer reached a steady state in 10 min.

3.2. Light induced water permeation through disperse red 1 modified membranes

The light induced water permeation through membranes was next examined. At the beginning, the non-modified PTFE (original PTFE) membrane was tested. A droplet of 0.5 mL of distilled water was put on the central area of the membrane as shown in Fig. 3, and the visible light (from 385 to 740 nm in wavelength) was irradiated to the whole water. After 1 h irradiation, water was found neither on the bottom of the petri dish under the membrane (permeated water) nor on the undersurface of the watch glass above the membrane (vaporized water). The volume of the water remained on the PTFE membrane was approximately 0.5 mL to indicate the complete recovery of the water put on the membrane. Thus, no permeation of water through the non-modified PTFE membrane occurred even under the visible light irradiation.

Table 1
Water permeation and desalination under visible light irradiation.[a]

Membrane	Under membrane (μL)	Above membrane (μL)	Remain on membrane (mL)	Electric conductivity (μS/cm)
Memb-1	18	4	0.47	–
Memb-1[b]	9	<2	0.49	–
Memb-1[c]	66	16	0.41	–
Memb-2	18	5	0.45	–
Memb-3	6	<2	0.49	–
Memb-4	29	12	0.43	–
Memb-1[d]	18	6	0.46	92 (<0.01)[g]
Memb-1[e]	30	5	0.43	–
Memb-1[d,e]	26	5	0.45	87 (<0.01)[g]
Memb-1[e,f]	32	5	0.43	54

[a] 0.5 mL of deionized water was put on membrane. Irradiation of visible light with wavelength from 385 to 740 nm for 1 h.
[b] Irradiation for 0.5 h.
[c] Irradiation for 3 h.
[d] 3.5% NaCl solution was used.
[e] Irradiation from a solar simulator at 1 SUN.
[f] Artificial seawater obtained from MARINE ART SF-1 was used.
[g] Concentration of NaCl (%).

Next, the DR1 modified PTFE membranes were applied to the light induced water membrane permeation. The results are summarized in Table 1. When no irradiation (in dark place) and the irradiation of visible light of 440 nm controlled by a band pass filter were used for 1 h, neither the permeated water nor the vaporized water was observed and nearly 0.5 mL of water was remained on the membrane. Moreover, no temperature elevation of the water was observed in both cases. Thus, no irradiation and the irradiation of the light that isomerizes DR1 only from trans to cis isomer had no effect for the water permeation through the membrane. On the other hand, after 1 h irradiation of visible light with wavelength from 385 to 740 nm, the volume of the water remained on the membrane decreased to approximately 0.47 mL (470 μL) and the temperature of the water was elevated slightly (about 4 °C increase). The content of DR1 in the remained water was <0.1 ppb to indicate no leaching of DR1 from the membrane. As mentioned in the introduction part, DR1 is a water-insoluble azobenzene dye. Water dews were found both on the bottom of the petri dish formed by the water permeation of the membrane (permeated water) and on the undersurface of the watch glass by the vaporization (vaporized water). The volumes of the permeated and vaporized waters were approximately 18 and 4 μL, respectively. No DR1 was detected even in the permeated and vaporized waters according to spectrometer analyses.

The light irradiation for 0.5 h and 3 h produced 9 and 66 μL of waters under the membrane, respectively. The volume of the permeated water
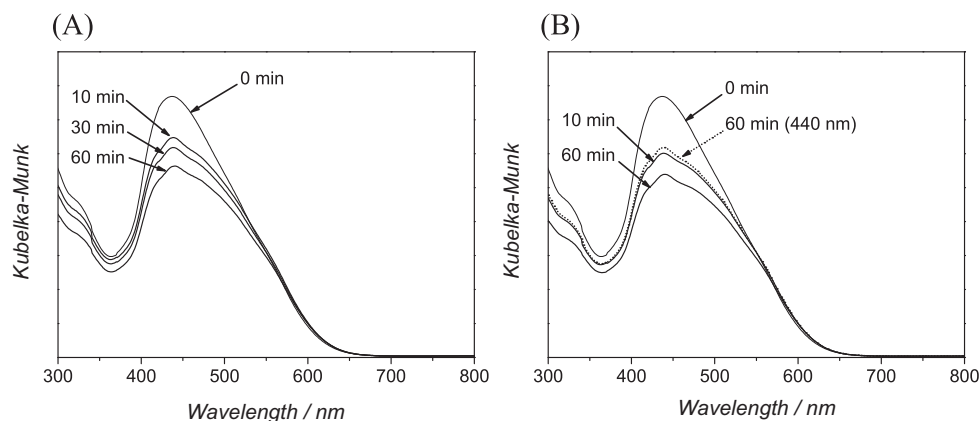
Fig. 7. (A) Diffuse reflectance spectra of DR1 modified PTFE membrane (**Memb-1**) under the irradiation of visible light with wavelength of 440 nm (Kubelka-Munk). (B) Diffuse reflectance spectra of DR1 modified PTFE membrane (**Memb-1**) under the irradiation of visible light with wavelength of 385–740 nm or 440 nm (dot-line) (Kubelka-Munk).

increased basically with the irradiation time. However, the temperature elevation of the water remained on the membrane was only 6 °C even after 3 h irradiation. The reproducibility of the water permeation was verified by the repeated experiments of 1 h irradiation. In five trials, the volumes of the permeated and vaporized waters were in the range of 16–21 μL and 4–7 μL, respectively. No deterioration of the permeation ability occurred in these repeated experiments. The DR1 modified membrane obtained from a PTFE membrane with a larger pore (3.0 μm; **Memb-2**) resulted in the similar result to **Memb-1**. The pore size of the PTFE membrane is unlikely to be an important factor in this membrane permeation. On the other hand, when the DR1 modified PTFE membrane prepared with a diluted solution of DR1 (**Memb-3**) was used (The color was lighter than that of **Memb-1** to show less DR1 on the membrane as shown in Fig. 5C.), the volumes of the permeated and vaporized waters decreased to 6 and 1.5 μL, respectively. The double modification of DR1 to PTFE membrane (**Memb-4**) improved the water penetration ability to increase the volume of the permeated water from 18 to 29 μL. Thus, the modification manner of DR1 on PTFE membrane was a significant factor for the performance of the light induced water permeation.

DR1 modified PES membrane (**Memb-5**) was also tried to the membrane permeation of water. When 0.5 mL of distilled water was put on this membrane, the water gradually seeped into the membrane to spread to the whole membrane after a period of time, probably because PES membrane is generally hydrophilic. After 1 h in dark place, a certain volume of water was found between the membrane and the Teflon holding ring platform (see Fig. 3). This water was thought to penetrate through the membrane naturally, while no water was observed between the PTFE membrane and the ring platform. This PES membrane could not prevent the natural dropping-down of water through the membrane, which must be avoided for preventing the contamination of the purified water with raw water. Therefore, the light induced membrane permeation using the DR1 modified PES membrane (**Memb-5**) was not tested. The employment of hydrophobic membrane must be essential for the light induced membrane permeation.

3.3. Light induced desalination with disperse red 1 modified PTFE membranes

Water desalination using the DR1 modified PTFE membrane was next examined. 3.5% NaCl aqueous solution (0.5 mL) was put on the DR1 modified PTFE membrane (**Memb-1**), and the visible light with wavelength from 385 to 740 nm was irradiated. After 1 h, about 18 and 6 μL of waters were observed both on the bottom of the petri dish and on the undersurface of the watch glass. Approximately 0.46 mL of the NaCl solution was remained on the membrane. These results were nearly the same as those using distilled water. The estimated value of the electric conductivity of the permeated water under the membrane was 92 μS/cm, which corresponded to <0.01% of NaCl concentration. The purity of the water recovered under the membrane reached a high enough level of freshwater (<0.05% NaCl). Thus, the DR1 modified PTFE membrane accomplished the desalination of the NaCl solution by the visible light irradiation. This light induced permeation of the NaCl solution was repeated three more times without washing the membrane (NaCl solution on the membrane was replaced in each case). The results in these three experiments were in the same ranges as the first experiment.

The mechanism of the water permeation by light irradiation is thought to be similar to the previous case [22]. The irradiated light causes the repetitive photo isomerization of DR1 between its trans and cis isomer. The molecular motion of DR1 induced by the photo isomerization activates water molecule located near DR1 on PTFE membrane to promote their evaporation. Finally, the water vapor penetrates the pore of PTFE membrane. In this study, the employments both of PTFE membrane and DR1 evolved this light induced water permeation and desalination system. The hydrophobic PTFE membrane efficiently rejected the natural penetration of water through the membrane and DR1 that photo-isomerizes by the light with wavelength of >440 nm enables the utilization of visible light. As the permeated water through the membrane is produced via water vapor, the recovered water under the membrane was purified and desalinated.

This membrane permeation and the desalination of water is different from the common water evaporation systems like solar still [12, 13], because the treated water could be readily collected under the membrane. In addition, as the temperature elevation of the water on membrane was modest as mentioned above (up to 6 °C increase), the mechanism of water evaporation on the DR1 modified membranes using visible light is different from that of light-to-heat conversion materials, because the materials rapidly elevate the temperature of water to produce steam [5–11]. The water treatment using the DR1 modified PTFE membranes resembles the process of membrane distillation [29–35], especially air-gap membrane distillation [34,35]. In the membrane distillation, the permeation of water vapor through hydrophobic membrane desalinates raw water, where the inhibition of the penetration of liquid water by hydrophobic membrane is a key function. While the raw water is often heated by artificial energy in common membrane distillation [29–35], solar energy is utilized in some recent systems, where heated water is produced in solar thermal systems separated from the membrane distillation part [32,33]. To the contrary, the membrane permeation in this study employed light energy directly in the membrane process. The droplet of raw water on the DR1 modified membrane was exposed directly to the irradiated light. Therefore, the total water treatment system can be simplified and is suitable for the direct use of solar light energy.

3.4. Seawater desalination with PTFE membranes using solar simulator

The wavelength and intensity of the irradiated light controlled by the VIS mirror module is approximately constant from 400 to 750 nm in wavelength, which is apparently different from real solar light on the surface of the ground. Then, a simulated solar light irradiated from a solar simulator (XEF-300, SAN-EI ELECTRIC CO., LTD.) was used for the light induced membrane permeation of water, because a goal of this research is seawater desalination using real solar light free from fossil fuel energy. The simulated solar light was irradiated to 0.5 mL of distilled water on the DR1 modified PTFE membrane (**Memb-1**) at 1 SUN. After 1 h irradiation, 30 μL of water, which was much more than that with the visible light (from 385 to 740 nm), was found on the petri dish under the membrane. As shown in Fig. 6, the absorption range of the DR1 modified PTFE membrane is suitable for the utilization of solar light. When the solar light was employed to the permeation of 3.5% NaCl solution, 26 μL of water was obtained under the membrane. The electric conductivity of the permeated water was 87 μS/cm and the concentration of NaCl was <0.01%. As the salinity of the water is equivalent to fresh water, the desalination of the NaCl solution using the simulated solar light certainly succeeded. This desalination experiment was repeated totally five times without washing the membrane in the same manner as that described above. In all five experiments, the volumes of the permeated waters were within the range of 22–26 μL, and their salinities were <0.01%. Thus, the desalination process is repeatable with no obvious deterioration of the performance of the membrane. Fig. 8 illustrates the scanning electron microscope (SEM) images of original PTFE membrane, DR1 modified PTFE membrane before use, and DR1 modified PTFE membrane after the utilization for the repeated permeation of NaCl solution. There are no clear differences among these three images. The modification of DR1 to the PTFE membrane did not change the morphology of the membrane from Fig. 8A and B. In the image of the used membrane (Fig. 8C), no observable fouling materials were found on the membrane. This membrane desalination effectively suppressed the salt fouling to achieve no deterioration of the membrane performance.

(A) (B) (C)
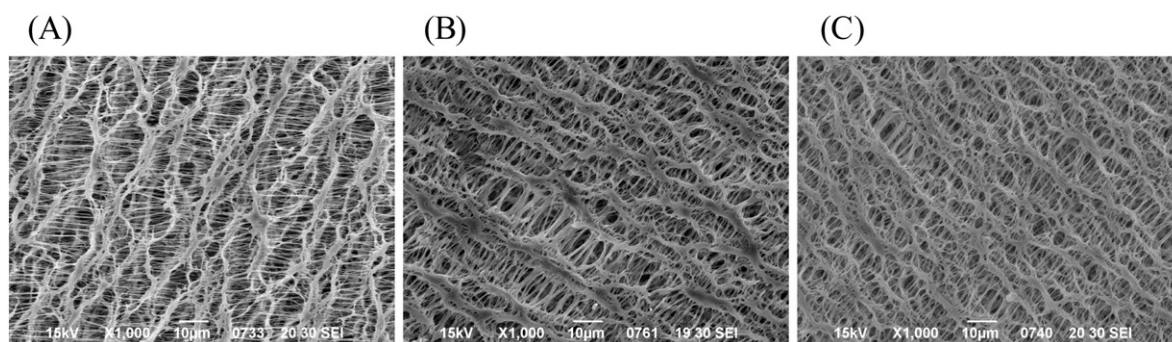
Fig. 8. SEM images of PTFE membranes. (A) Original PTFE membrane, (B) DR1 modified PTFE membrane before used, and (C) DR1 modified PTFE membrane after the use for the repeated permeation of NaCl solution.

At the end, an artificial seawater obtained with MARINE ART SF-1, whose composition formula of minerals is the same as that of real seawater [28], was employed. This artificial seawater well duplicates real surface seawater. For example, the pH value of the artificial seawater was 8.1 that is the same as that of current real surface seawater [36]. On the other hand, 3.5% NaCl solution used in this study had a pH value of 5.4. As listed in Table 1, the volume of the permeated water was 32 μL by the irradiation of the simulated solar light. The electric conductivity of the permeated water was 54 μS/cm to be desalinated to purified fresh water. In the same repeated experiments as the NaCl solution, the volumes of the permeated water and their electric conductivity were within the range of 32–36 μL and of 39–54 μS/cm, respectively. Thus, the desalination of an artificial seawater succeeded by a simulated solar light without deterioration.

4. Conclusions

This paper reports the light induced water permeation using DR1 (disperse red 1) modified PTFE membranes. Hydrophobic PTFE membrane prevents the natural infiltration of raw water into the membrane completely, while it can happen in anodized alumina membrane reported before [22]. DR1 conducts its repetitive photo isomerization only by visible light, requiring no UV light that is scarcely contained in solar light. The permeation of distilled water through the DR1 modified PTFE membrane took place under the irradiation of visible light (from 385 to 740 nm), while no penetration occurred without the light. 3.5% NaCl solution and an artificial seawater also permeated the membrane under the light irradiation, and the recovered water under the membrane was sufficiently desalinated. The electric conductivity and the concentration of NaCl of the permeated water were <100 μS/cm and 0.01%, respectively. As the salinity of freshwater is <0.05%, this light induced water permeation efficiently converted the NaCl solution to a desalinated freshwater. The water permeation and desalination were also accomplished by a simulated solar light, where the concentration of NaCl in the penetrated water decreased to <0.01% as well. In addition, the desalination of an artificial seawater to purified water was achieved by the light irradiation with a solar simulator. These results clearly show that the desalination process using solar light as a main energy source shown in Fig. 1 is realizable by the DR1 modified PTFE membrane. The most important advantage of the DR1 modified PTFE membranes is that the desalination of seawater as the most energy-requiring step is accomplished only by solar light energy, which extensively decreases the consumption of fossil fuels in the whole desalination process.

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