

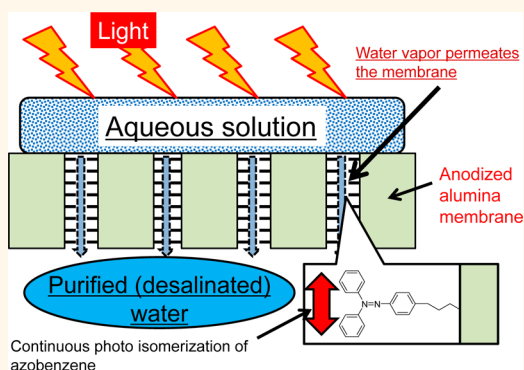
Photo Induced Membrane Separation for Water Purification and Desalination Using Azobenzene Modified Anodized Alumina Membranes

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ABSTRACT Water purification and desalination to produce end-use water are important agendas in 21st century, because the global water shortage is becoming increasingly serious. Those processes using light energy, especially solar energy, without the consumption of fossil fuels are desired for creating sustainable society.

For these earth-friendly water treatments, nanoporous materials and membranes are expected to provide new technologies. We have reported before that the repetitive photo isomerization of azobenzene groups between the trans and cis isomers induced by the simultaneous irradiation of UV and visible lights accelerates the molecular movement of nearby molecules in nanoporous materials. After further studies, we recently found that the permeation of water through azobenzene modified anodized alumina membranes as a photo responsive nanoporous membrane was achieved by the simultaneous irradiation of UV and visible lights, while no water penetration occurred under no light, only single UV or visible light. The photo induced permeation of water was promoted by the vaporization of water with the repetitive photo isomerization of azobenzene. This membrane permeation achieved the purification of water solutions, because dye molecules and a protein dissolved in aqueous solutions were not involved in the photo induced penetrated water. When 3.5% of sodium chloride solution as model seawater was employed for this membrane separation, the salt content of the permeated water was less than 0.01% to accomplish the complete desalination of seawater.



KEYWORDS: azobenzene · photo isomerization · anodized alumina membranes · membrane separation · water purification · seawater desalination

The production of end-use waters suitable for drinking, industry and agriculture from contaminated and untreated waters is an essential technology for resolving the global water shortage problem. Recently, the production of potable freshwater from seawater is also becoming an important agenda.^{1–3} Since these problems are closely related to the global warming by carbon dioxide emission, the energy used for these water treatment must be free from fossil fuel. Although the utilization of solar light energy, for example, is a strongly desired approach, the applications of light energy to the water treatment have been limited to photocatalyst processes decomposing impurities and undesired substances in water to harmless materials

without their recovery.^{4–8} In the case of seawater desalination, the light energy plays only supporting roles in the distillation⁹ and the membrane separation^{9–12} that require a large amount of energy for heating or pressurizing water.^{13–15}

Nanoporous materials and membranes are considered to have enormous potential for creating new technologies toward the global water shortage problem.^{16,17} The development of the reverse osmosis (RO) membrane technology to water treatment is also promoted by the chemistry and science of nanoporous materials and membranes.^{9–15} On the other hand, we reported before that the structural changes of the organic substituents loaded into nano-sized pore voids effectively control the

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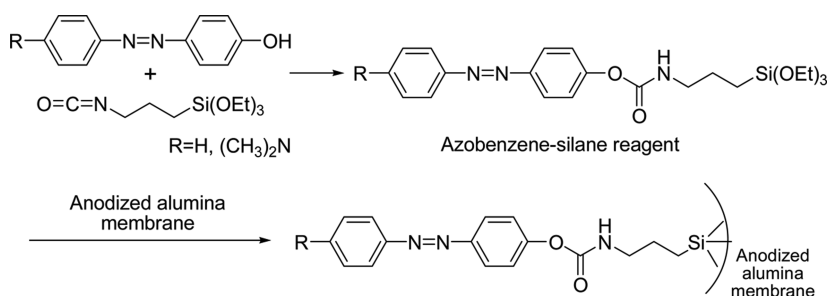


Figure 1. Preparation processes of azobenzene modified anodized alumina membranes.

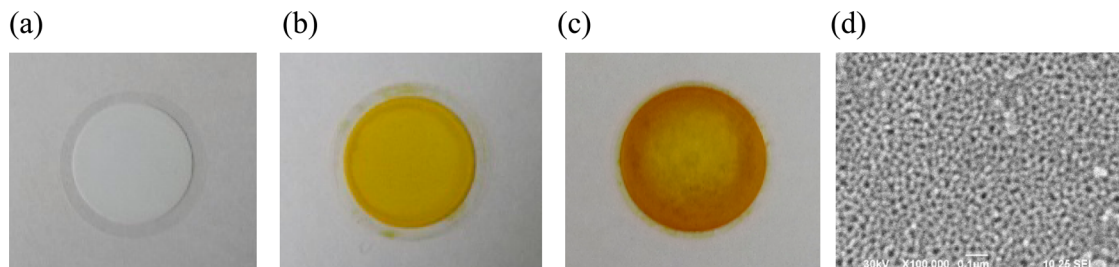


Figure 2. (a–c) Images of the anodized alumina membranes. (a) Membrane M-0, (b) membrane M-1, (c) membrane M-2. (d) SEM image of membrane M-1.

movements of molecules inside the nanopores.^{18–22} Especially, the simultaneous irradiation of UV and visible lights to grafted azobenzene substituents induces its consecutive motion between the *trans* and *cis* isomers to accelerate the release of molecules from mesoporous silica²⁰ and to increase the flow rate of the organic solvents in silica gel column.²¹ These results suggest us to apply the azobenzene isomerization technique to membrane separation. Anodized alumina membranes are thin porous alumina membranes with ordered nanopore arrays prepared electrochemically from aluminum metal, which are expected to contribute new technologies of water treatment.^{23–26} Here, we report the photo induced permeation of water through azobenzene modified anodized alumina membranes, where the purification of the aqueous solutions dissolving dye and protein was achieved. This membrane separation also enabled the seawater desalination to produce freshwater.^{1–3,27,28}

RESULTS AND DISCUSSION

When we used the azobenzene-silane reagents shown in Figure 1, whose UV–vis spectra are provided in Supporting Information (Figure S1), the azobenzene substituents were grafted to an anodized alumina membrane (Whatman “Anodisc 25”) by the condensation of the ethoxy group of the reagents and the alumina surface. The images of the membranes thus prepared are shown in Figure 2a–c. While the original alumina membrane **M-0** was white (Figure 2a), the membranes **M-1** and **M-2** with the azobenzene silane substituents [**M-1**, R=H; **M-2**, R=(CH₃)₂N in Figure 1] had dark yellow or orange color (Figure 2b,c). A SEM image of the membrane **M-1** (Figure 2d), which shows

the arranged nanopores approximately 20 nm in diameter typically observed in anodized alumina membranes, indicated that the pore structure of the membrane was maintained even after the grafting treatment. Figure 3 indicates the Kubelka–Munk function of the diffuse reflectance UV–vis spectra of the membrane **M-1**. The line i in Figure 3a certainly revealed the successful grafting of the azobenzene group onto the membrane. When UV light of 350 nm in wavelength was irradiated to the membrane **M-1** for 15 min, the absorption at about 340 nm decreased and adversely that at about 440 nm increased (line ii). These changes indicated that the *trans*-azobenzene tethered on the membrane was isomerized to the *cis*-isomer. Although this spectrum was nearly unchanged in dark place for 30 min (line iii), the irradiation of visible light of 440 nm for 15 min turned the spectrum back to the original one completely (not indicated in Figure 3a due to the complete overlap with the line i). Thus, the rapid repetitive photo isomerization between the *trans*- and *cis*-azobenzene in the membrane **M-1** requires the respective lights suitable for the each isomerization. When UV and visible lights from about 300 to 600 nm controlled by a mirror module were irradiated to the membrane **M-1**, the resulting spectrum (line iv) became intermediate between those of no irradiation (line i) and after UV irradiation for 15 min (line ii) as shown in Figure 3b. It is thought that the repetitive photo isomerization of the azobenzene between the two isomers^{29–32} took place smoothly on the anodized alumina membrane under the simultaneous irradiation of the UV and visible lights. On the other hand, there were no clear changes in the infrared spectra of the membrane **M-1** under various irradiation conditions.

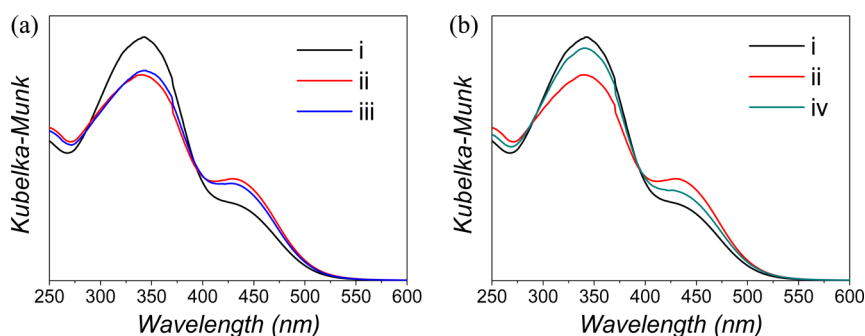


Figure 3. (a) Diffuse reflectance UV–vis spectra (Kubelka–Munk function) of the membrane M-1 under various photo irradiations. (i) No irradiation, (ii) UV (350 nm) for 15 min, (iii) in dark place for 30 min after ii. (b) Diffuse reflectance UV–vis spectra (Kubelka–Munk function) of the membrane M-1 under various photo irradiations. (i) No irradiation, (ii) UV (350 nm) for 15 min, (iv) UV + visible (300–600 nm) for 15 min.

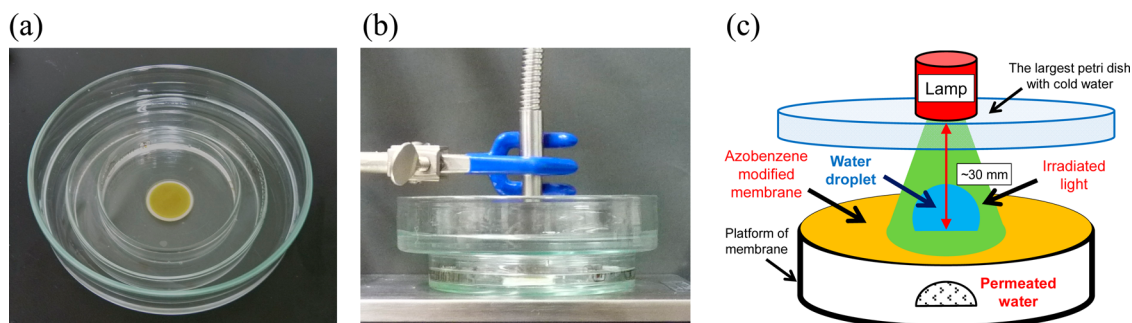


Figure 4. (a and b) Pictures of the apparatus system of the membrane permeation experiments. (c) Pattern diagram of the membrane permeation of water droplet under photo irradiation.

The absorption of carbamate group at 1694 cm^{-1} and those of azobenzene group at 1557 and 1482 cm^{-1} were similar in all spectra of the membrane **M-1** before irradiation, after UV light irradiation, after visible light irradiation and after UV and visible lights irradiation as illustrated in Supporting Information Figure S2.

Next, the permeation of deionized water through the membranes was examined using the experimental installation shown in Figure 4. The membrane on a ring platform was put into the smallest glass Petri dish (borosilicate glass), which was packed in larger Petri dishes as shown in Figure 4a. The light from the lamp was exposed to a water droplet through the Petri dish with cool water (about 5 mm thick) for preventing the heat conduction from the lamp (see Figure 4b,c). The distance between the lamp bottom and the membrane was about 30 mm in all experiments. Table 1 summarized the results of the contact angles of water droplets on the membranes and the volumes of the permeated water under various irradiation conditions. A $10\ \mu\text{L}$ water droplet put onto the original membrane **M-0** immediately spread over the surface to show a low contact angle of less than 5° . When UV and visible lights (from 300 to 600 nm in wavelength) were irradiated for 10 min to the widespread water, a slight amount of water (less than $0.5\ \mu\text{L}$) was found under the membrane **M-0** probably because of the natural drop of the impregnated water through the membrane.

TABLE 1. Contact Angles of Water Droplets and Water Permeation Volumes through Azobenzene Modified Anodized Alumina Membranes under Light Irradiations

membrane	R in Figure 1	contact angle (deg) ^a	irradiated light (nm) ^b	volume (μL) ^c
M-0	—	<5	300–600	0.5
M-1	H	104	300–600	2.1
M-1	H	104	385–740	1.2
M-1	H	104	~350	0.0
M-1	H	104	~440	0.0
M-2	Me ₂ N	75	300–600	1.8
M-2	Me ₂ N	75	385–740	2.0
M-3	(Octadecyl)	112	300–600	0.0

^a Measured by half angle method with $10\ \mu\text{L}$ droplet. ^b Controlled by mirror modules and bandpass filters. ^c After the irradiation for 10 min to $10\ \mu\text{L}$ droplet.

The azobenzene modified membrane **M-1** was water repellent having a high contact angle of about 104° as illustrated in Figure 5a. The repelled water droplet did not permeate the membrane naturally in dark place at least for 3 h. The individual irradiation of the UV light (around 350 nm) or the visible light (around 440 nm) to the water droplet for more than 15 min resulted in no penetration of water and certain volumes of the droplets were still remained on the membrane in both cases. On the other hand, the simultaneous irradiation of the UV and visible lights (from 300 to 600 nm) for

10 min achieved the permeation of approximately 2.1 μL of water through the membrane with the complete disappearance of water on the membrane. Therefore, the water permeation of the azobenzene modified membrane was triggered by the simultaneous photo irradiation. These observations are well consistent with our previous results in azobenzene modified mesoporous silica and silica gel column, where the simultaneous irradiation of the UV and visible lights is the most active for increasing molecular movement.^{20,21} When this experiment was repeated 10 times, equivalent results were produced in all experiments (1.9–2.2 μL). The photo induce water permeation had a high repeatability and the azobenzene modified membrane had a good stability to the light irradiation. The area where the penetrated water was found on the Petri dish under the membrane **M-1** (Figure 5b,c) was approximately the same as that of the water droplet on the membrane. In the cases of shorter irradiation for 2 or 5 min, the volumes of the permeated water were 1.1 and 1.4 μL with about 4 and 2 μL of water remained on the membrane, respectively. Water did not appear to infiltrate into the membrane, and water dews were also found on the undersurface of the largest Petri dish just above the droplet on the membrane. The permeation and the evaporation of water caused the decrease and disappearance of the water droplet in the case of the membrane **M-1** with the UV and visible lights irradiation.

The membrane with dimethylaminoazobenzene group **M-2** was also active for the photo induced permeation of water. Approximately 1.8 μL of water passed through the membrane by the simultaneous irradiation of the UV and visible lights for 10 min, while no water remained on the membrane. Since the dimethylaminoazobenzene group requires no UV light for the photo isomerization (see Supporting Information Figure S1b), only visible light (from 385 to 740 nm in wavelength) was irradiated using another mirror module. After 10 min irradiation, about 2.0 μL of water was penetrated, where water was still observed on the membrane. The single visible light irradiation slowed the disappearance of water. When this visible light (385–740 nm) was used for the water permeation with the membrane **M-1**, a lower volume of water (1.2 μL) was infiltrated than the irradiation of the UV and visible

lights, because the photo isomerization of the *trans*-azobenzene in the membrane **M-1** did not fully progressed by the visible light irradiation. However, when *n*-octadecyl group modified anodized alumina membrane (membrane **M-3**) with a higher water repellency (contact angle 112°) was employed, all three light irradiations including the simultaneous irradiation resulted in no water penetration and the water on the membrane was mostly recovered (more than 80%). Even the evaporation of water from the droplet on the membrane **M-3** scarcely occurred. Therefore, it is concluded that the photo induced water permeation took place only when the azobenzene groups were grafted on the membrane.

Since light can rigorously regulate the irradiation area, the region where the water permeation through the membrane occurs can be controlled by the light exposure. Two water droplets (10 μL each) were placed on the same membrane (**M-1**) (Figure 6a) and the UV and visible lights (300–600 nm) were irradiated to the left droplet for 15 min, while the right droplet was covered with a thick black paper for protecting from the light exposure. In this case, the water permeation was only observed just under the left droplet without residual water on the membrane, while no water was found under the membrane and the right droplet was still remained on the membrane (Figure 6b). Even in the left–right reversal test, the water penetration was observed only under the droplet with the light irradiation. Thus, the area of the membrane permeation can be controlled by the light irradiation perfectly.

The high water repellency of the azobenzene modified anodized alumina membrane inhibited the natural

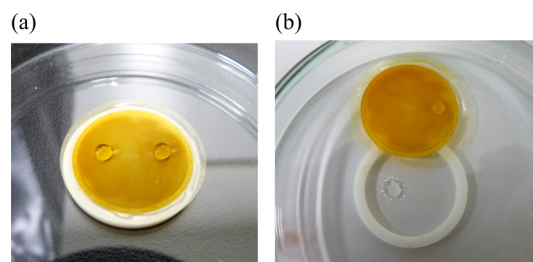


Figure 6. (a) Picture of two water droplets on the membrane **M-1**. (b) Picture of the water permeated when the UV and visible lights were irradiated to the left droplet and the right droplet was masked with black paper.

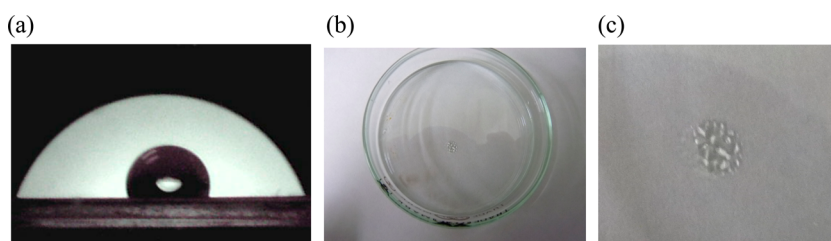


Figure 5. (a) Image of a 10 μL water droplet on the azobenzene modified anodized alumina membrane **M-1**. (b and c) Pictures of the water dews observed on the Petri dish just under the membrane **M-1**; (b) picture with Petri dish and (c) close-up picture.

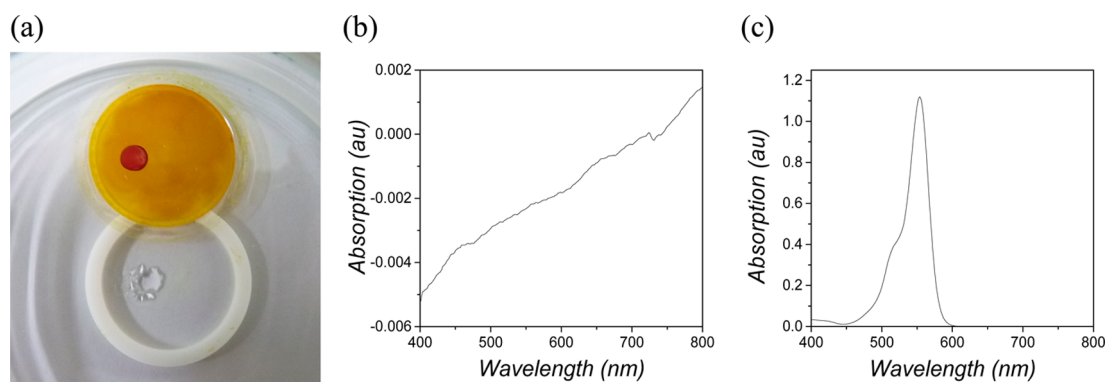


Figure 7. (a) Picture of the permeated water from rhodamine B solution through the membrane M-1 after the UV and visible lights irradiation. (b) Visible spectrum of the permeated water from the rhodamine B solution. (c) Visible spectrum of 0.01 mM solution of rhodamine B.

permeation of liquid water through the nanopores of the membrane by the surface tension of water. On the other hand, when liquid water evaporates into water steam, it is thought that the water penetration through the membrane is not suppressed due to the lack of surface tension of steam. This water steam permeation of the azobenzene modified membrane resembles the distillation of water rather than the membrane separation in principle. Then, the membrane permeation of aqueous solutions dissolving nonvolatile materials is examined, because the distillation of water must achieve the separation of those materials from water. The aqueous solution of rhodamine B, which is often used as a model water contaminant in the water purification researches,³³ was tested for the membrane separation experiment. An aqueous solution of rhodamine B (1 mM, 10 μL) was put on the membrane **M-1** and the UV and visible lights were irradiated simultaneously. After 15 min, the colorless transparent water dews (approximately 3.0 μL) were found under the membrane (Figure 7a). In the visible spectrum of this penetrated water shown in Figure 7b, no absorption of rhodamine B around 554 nm in wavelength (Figure 7c) was observed to show that rhodamine B was separated completely. The rhodamine B solution on the membrane disappeared after the test, and a dark red spot of the same size as the water droplet was found as indicated in Figure 7a. Even when the aqueous solution of methylene blue as another common model contaminant molecule was employed for the same examination, no absorptions of methylene blue was detected in the penetrated water (about 3.0 μL) as shown in Supporting Information Figure S3 and the dark blue spot was observed on the resulting membrane. A protein, lysozyme, could be also separated from the aqueous solution using this membrane separation method. After the UV and visible lights irradiation to the aqueous solution of lysozyme (5 mg/mL, 10 μL) on the membrane **M-1** for 15 min, about 2.2 μL of water penetrated through the membrane, which contained no lysozyme according to the UV spectrum

of the solution (see Supporting Information Figure S4). After these separation treatments, the dye molecules and lysozyme could be mostly recovered from the membranes by water extraction. Thus, the membrane separation process perfectly separated the components dissolved in water, revealing that the photo induced water permeation arose from the vaporization of water on the azobenzene modified anodized membrane.

We^{20,21} and Angelos *et al.*^{31,32} have reported that the azobenzene group in nanopores photo isomerizing continuously in picosecond scale^{34–36} works as a molecular impeller to accelerate the movement of nearby molecules. In this membrane permeation, the continuous photo isomerization of azobenzene groups induced by the simultaneous irradiation of two kinds of lights for the respective isomerization elicits the high-speed movement of the azobenzene group in the nanosized pores of the anodized alumina membrane. This intense motion of the azobenzene group efficiently activates the molecular movement of water, because they are confined in nanopores, eventually achieving the vaporization of water and their permeation through the membrane. The exposure of the UV and visible lights to the membrane **M-1** without water droplet elevated the temperature of the surface from 20 to 28 $^{\circ}\text{C}$ after 15 min. This moderate warming is unlikely to be sufficient for water evaporation under atmospheric pressure. In addition, when the membrane **M-1** with 10 μL of deionized water was heated at 50 $^{\circ}\text{C}$ for 15 min, no water was found under the membrane and approximately 4.6 μL of water was still remained on the membrane. As mentioned before, the irradiation of the UV and visible lights to a water droplet (10 μL) on the membrane **M-1** achieved its complete disappearance after 10 min. These results obviously indicate that the evaporation of water is not simply caused by the heating effect of the molecular motion of the azobenzene group. It is assumed that the movement of azobenzene also works as molecular “fan” to promote water evaporation by “blower” effect.

These heating and blowing effects produced water steam in the channel of the anodized alumina membrane to elicit the water permeation. Since nonvolatile elements could not vaporize, the effective purification of the aqueous solutions dissolving dyes and lysozyme were accomplished.

This membrane separation technique could be applied to seawater desalination. In this experiment, 1 mL of 3.5% sodium chloride aqueous solution as a simulated seawater was filled over the membranes. This volume was nearly the maximum amount of water put on the membrane. When the original membrane **M-0** was used for the desalination of the sodium chloride solution without the photo irradiation for 2 h, 0.24 mL of water found under the membrane had the electric conductance over the detection limit of our conductivity meter (20 mS/cm, salt content 1.1%). The sodium chloride solution dripped off through the anodized alumina membrane naturally, and no desalination occurred. On the other hand, no drop down of the sodium chloride solution was observed when the solution was placed on the membrane **M-1** for 2 h in dark place. After the UV and visible lights irradiation for 2 h to the solution, approximately 0.18 mL of water was collected under the membrane. The electric conductance of the penetrated solution was 17 μ S/cm, which was converted to less than 0.01% salt content. This water can be considered as freshwater, because the salt concentration of potable freshwater is generally less than 0.05% (10 mM).^{12,37} We attempted repeated use of the membrane after washing with fresh deionized water. Although the volume of the permeated water decreased to about 90% in the second experiment, about 80% of water compared with the first experiment was penetrated even after 5 times repetition. All the salt contents of the permeated water were less than 0.01%. In SEM images of the membrane used for the desalination experiment 5 times (Supporting Information Figure S5), a number of small particles were found and some nanopore channels of the membrane looked clogged. These changes of the membrane were thought to be due to the deposition of sodium chloride during the desalination process. However, the major part of the channels in the membrane appeared to be still available for seawater desalination. The membrane **M-3** with octadecyl group was powerless even for the permeation of the sodium chloride solution, and no water was detected under the membrane after the simultaneous irradiation for 2 h. Since the utilization of solar light energy to the seawater desalination is expected to reduce the consumption of fossil fuels,^{13–15} the desalination using only the visible light was attempted as well. When the membrane **M-2** with dimethylaminoazobenzene group was employed for the membrane separation under visible light irradiation (385–740 nm) for 2 h, approximately 0.022 mL of water was permeated. The electric

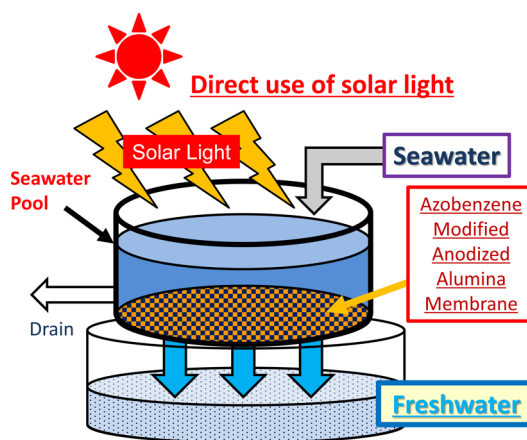


Figure 8. A proposed seawater desalination system using azobenzene modified anodized alumina membrane and solar light energy.

conductance of the water was estimated to be 67 μ S/cm corresponding to less than 0.01% salt content. Thus, these results revealed that this photo induced membrane separation can be applied to seawater desalination under the light energy including visible solar light.

Figure 8 illustrates an expected seawater desalination system using azobenzene modified anodized alumina membrane and solar light energy. Seawater is pumped from sea to a water pool, whose bottom was built up of the azobenzene modified anodized alumina membrane. The seawater in the pool is exposed to solar light directly, and freshwater is produced under the membrane by the photo induced permeation. This system is an advanced variation of direct solar desalination,^{13,38} and neither the energy from fossil fuel nor the conversion of solar energy are required for the process of seawater desalination. Therefore, the total energy efficiency of this system is expected to become considerably higher than desalination processes by distillation and reverse osmosis membrane. Although the mechanical strength of the alumina membrane and the chemical stability of azobenzene group are still problems to be resolved, we are now addressing the improvement of the azobenzene modified membrane system for practical seawater desalination.

CONCLUSIONS

In conclusion, water permeated the azobenzene modified anodized alumina membranes under the irradiation of UV and visible lights at the same time. This water permeation occurred only when and where the lights were irradiated. During the irradiation of the lights producing both the isomerization of azobenzene from trans to cis and cis to trans isomers, the rapid movement of the azobenzene groups between the two isomers induced the vaporization of the liquid water, leading to the infiltration through the membranes.

When the aqueous solutions of dyes and lysozyme were used, no such additives were detected in the penetrated water. This water membrane separation process was also applied to the desalination of seawater. When 3.5% sodium chloride solution was employed, the salt contents of the recovered water under

the membranes were less than 0.01% that was regarded as drinkable freshwater. Thus, we found the technology of a photo induced membrane separation using the azobenzene modified anodized alumina membranes, which contributes to water purification and seawater desalination by solar energy.

MATERIALS AND METHODS

Azobenzene modified anodized alumina membranes (**M-1** and **M-2**) were prepared by the reaction scheme shown in Figure 1. The experimental procedures are as follows: 4-hydroxyazobenzene (0.217 g, 0.986 mmol) or 4-hydroxy-4'-dimethylaminoazobenzene (0.240 g, 0.995 mmol) was mixed with 3-(triethoxysilyl)propyl isocyanate (0.246 g, 0.994 mmol) in dry DMF (10 mL), and the resulting solution was heated at 150 °C for 24 h. The reaction was monitored by the disappearance of the infrared absorption of the isocyanate at 2272 cm^{-1} . These DMF solutions were directly used for the modification of anodized alumina membranes **M-0** (Whatman "Anodisc 25"; thickness, 60 μm ; diameter, 25 mm; main pore size, 0.02 μm). These anodized alumina membranes with the impregnated azobenzene silane reagents were allowed to stand still for more than 3 days at room temperature, and were heated at 120 °C for 24 h. The resulting membranes were immersed in acetone to eliminate the removal azobenzene silane reagents 3 or 4 times, until the reagents were not detected in the washed acetone solution of the UV-vis spectra. Finally, the membranes were dried at room temperature. *n*-Octadecyl group modified membrane (**M-3**) was prepared by the analogous procedure using *n*-octadecyltrimethoxysilane.

The absorption spectra of the azobenzene silane reagents 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 integrating sphere. The light irradiation was performed using a Xenon light source MAX-301 (300 W xenon lamp; Asahi Spectra Co. Ltd.) equipped with UV-vis mirror module (Irradiated light was controlled mainly from 300 to 600 nm in wavelength.) or VIS mirror module (controlled mainly from 385 to 740 nm in wavelength.). These modules were purposely used for removing near-infrared light. The simultaneous irradiation of UV and visible lights was carried out using the light source equipped with a mirror module without any bandpass filters. The individual UV (350 nm) or visible (440 nm) light irradiation was achieved by using the respective bandpass filters. Infrared spectra were recorded using a Perkin-Elmer Spectrum One spectrometer. Anodized alumina membranes were directly measured by transmittance method. Since infrared absorption of alumina at wavenumbers less than 1200 cm^{-1} was strong, spectra at wavenumbers higher than 1200 cm^{-1} were analyzed. The contact angles of water on the membranes were measured by a contact angle meter of EXCIMER Inc., the Model Simage mini, using a half angle method, where 10 μL of water droplets was used. SEM images were obtained by JEOL JSM-6390 electron microscope.

The membrane permeation experiments of water were performed with the apparatus system shown in Figure 4. The membrane on a ring platform (1.5 mm thick) was put into the smallest glass Petri dish that was cooled by ice water in a larger Petri dish. On the top of the set of these two Petri dishes, the largest Petri dish was placed, which contained cool water (about 5 mm thick) for preventing the heat conduction from the lamp (see Figure 4a,b). All Petri dishes used in the experiments are made of borosilicate glass. Figure 4c illustrated the pattern diagram of the light irradiation experiment to 10 μL water droplet on the membrane. The distance between the lamp bottom and the membrane was fixed to about 30 mm in all experiments. After the irradiation, the liquids on the smallest Petri dish under the membrane were collected by a 10 μL microsyringe to estimate their volumes. On the other hand, the

volumes of liquids remained on the membranes after the irradiation could not be accurately measured because of the risk for breaking the membranes by the needle of the microsyringe. Even in the experiments of the membrane separation of aqueous solutions, 10 μL of the respective solutions was employed. The concentrations of aqueous solutions with rhodamine B and methylene blue were 1 mM, and that of lysozyme was 5 mg/mL. After estimating the volumes of the penetrated waters under the membrane, 3 mL of fresh deionized water was added to these recovered water for visible spectrometry measurement with JASCO V-530 spectrometer.

In the desalination of sodium chloride solution, a simulated seawater (3.5% sodium chloride solution) was prepared from a commercially available sodium chloride (special grade) and deionized water (electric conductivity, 2 $\mu\text{S}/\text{cm}$; salt content, <0.01%). One milliliter of the sodium chloride solution was spread over a membrane and the lights were irradiated to the whole area of the solution. After determining the volumes of the permeated water, the electric conductivity of the water and the concentration of the salt were analyzed by a conductance meter, B-771 LAQUAtwin compact conductivity meter (HORIBA, Ltd.). When the volume of the water was less than the minimum sample volume (0.12 mL), the bare essentials of fresh deionized water were added for the analysis of the electric conductivity. The electric conductivities of the water in these cases were estimated by the adjustment from the volumes of the additional deionized water.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: UV-vis spectra (absorption) of the azobenzene-silane reagents; infrared spectra of anodized alumina membranes; visible spectra of the permeated solution of the solutions with methylene blue and methylene blue solution after 100-fold dilution; UV spectra of the permeated solution of the lysozyme solution; SEM images of an azobenzene modified anodized alumina membrane after the seawater desalination experiment 5 times. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/nn505970n.

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