Light-response of N_2 Permeation Using Gold Colloid-coated Porous Glass Modified by Azo Derivative Including Thiol

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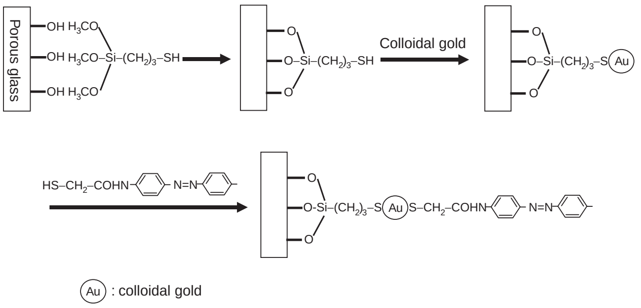
Photo responsive gas separation membrane modified by organic azo derivative including thiol group on the gold colloid-coated porous glass tube was shown that the nitrogen gas permeance was increased by the stimulation of UV light and stopped the permeation by stopping the irradiation.

It is well known that the structure of azobenzene derivatives show photoreversible cis–trans isomerization is drastically changed.[1,2] Expectedly, this would lead to the possibility of controlling the chemical functions by "on–off switching" and several investigations considering this concept have been reported.[3–5] On the other hand, porous glass membrane which possesses sharp pore size distribution are now actively investigated because of the higher gas selectivity.[6] In the previous study,[7] attempts to control the "on–off switching" the gas permeation by porous glass modified by azo derivative were successful. The modification amount of organic compound, however, was theoretically very small compared with that of silanol groups on the surface. Thus, a definite response of "on–off switching" by stimulation can be achieved when the modification amount is increased. In this study, preparation of porous glass membrane surface modified by thiol group, coated by colloidal gold, and then the suface modification by azo derivative including thiol group again was carried out for use of gas flow controlling. Furthermore, a control of the gas permeability by photoinduced cis–trans switching property of the compound under UV light irradiation or not was investigated.

Tubular porous glass membrane have been prepared and the gas permeance measurement at 300 K have been carried out according to the procedure reported elsewhere.[8] The chemicals which were used in this study were purchased either from Kishida Chemical Co., Ltd. and Aldrich Inc. or used without any purification. The azo derivative, $HS–CH_2–COHN–C_6H_4N{=}NC_6H_5$, was condensed product of aminoazobenzene and thioglycolic acid. At first, as shown in Scheme 1, surface treated porous glass by 3-mercaptopropyltrimethoxysilane as a coupling agent was taken into the aqueous acidic gold(III) chloride solution at room temperature for 24 h. And then the gold-treated porous glass and $HS–CH_2–COHN–C_6H_4N{=}NC_6H_5$ in toluene were kept at room temperature for more than 24 h. Subsequently, the porous glass was refluxed in toluene for more than 24 h washed in toluene for several times. The azo modification membrane tube (one end was sealed by epoxy resin) was attached to the Pyrex glass tube by epoxy resin and then the support tube with the membrane was placed inside a stainless steel permeation cell with a silica window through a flange connection after drying at 348 K in vacuum for 1 h. Using the membrane prepared, gas permeance of the respective pure N_2 gas was measured by a mass flow meter. The single feed gas of N_2 was passed continuously outside of the membrane under the pressure of ca. 3.03×10^5 Pa (3.0 atm) at room temperature (300 K). The 350-nm light irradiation of Xe lamp (500 mW cm^{-2}) cut the visible light by glass filter was carried out from the quartz window and covering the window with a thick board performed the non-irradiation. The elemental analysis was carried out by CHN CORDER (MT-5, Yanaco) controlled by personal computer.



Scheme 1. The surface modification on the gold colloid-coated porous glass by azobenzene derivative including thiol.

The SEM images of the cross section of porous glass before and after attached the colloidal gold on the surface were shown in Figure 1. The surface before attached gold nanoparticles (the part of (c) in inset image) was very smooth but the surface after attached (the part of (a)) was very rough. The color of the porous glass before the gold treatment was semitransparent, however, the after was dark brown and the gold layer was not peeled off by scratching by nail. This indicated that the gold nanoparticles were chemically bonded on the porous glass surface. Finally, it was found that the thickness of the gold layer was approximately 1 μm from this cross section image.

In the previous work, using the modified membrane by

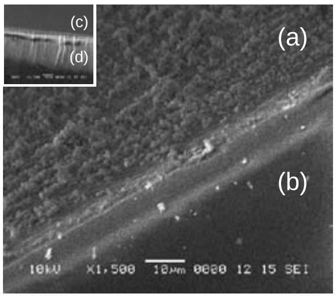


Figure 1. SEM images of the cross section of porous glass before (inset image, (c); outer surface and (d); cross section of porous glass) and after attached the colloidal gold on the thiol-modified porous glass surface ((a); outer surface and (b); cross section of porous glass).

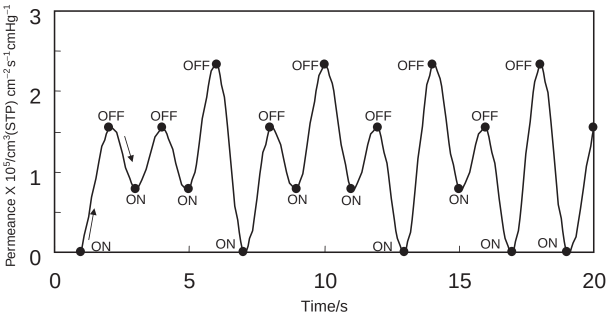


Figure 2. N_2 flow variation through the surface-modified porous glass (thiol–gold–azobenzene derivative including thiol group) under irradiation or non-irradiation of UV light under 350 nm.

11-[4-[(4-hexylphenyl)azo]phenoxy]undecanoic acid,[9] the changes of the N_2 and He flow amount before and after irradiation of Xe light were investigated at 300 K. The flow of each gas was slightly decreased during irradiation of Xe light and then the flow was increased by stopping the irradiation. These cycles could be continued for more than 30 times. Furthermore, there was no light response when similar experiments were considered using non-treated porous glass, porous glass treated by silane coupling agent only. The magnitude between increasing and decreasing the gas permeance, however, was only 2–3%. This difference is almost similar to that of adsorption and desorption of N_2 gas. Furthermore, the organic compound modification amount was only 0.2 mmol per gram of porous glass. Normally, the amount of the reactive silanol groups on 1 gram of porous glass is 0.8 mmol, thus the silanol on porous glass was remained 75% after the modification process. On the other hand, the change of the N_2 flow using modified porous glass by thiol–gold–azobenzene derivative including thiol group before and after irradiation of UV light were investigated at room temperature (300 K) and the result was shown in Figure 2. The flow of the N_2 gas was drastically increased by irradiation of UV light under 350 nm and stopped the flow by the stopping the irradiation. In addition, the response time was very fast than that of the membrane in the previous work. Furthermore, the behavior of the increasing and decreasing the N_2 gas flow was so reasonable because it seemed that the resistance of the N_2 gas permeance was lower under cis form. The surface modification amount of $HS–CH_2–COHN–C_6H_4N=NC_6H_5$ was ca. 0.4 mmol per gram of porous glass. Finally, the definite response of the N_2 gas flow or not was realized increasing the amount of azobenzene derivative including thiol group on the gold-coated porous glass surface.

The stability of the gas control by the membrane in dark and under irradiation with light was shown in Figure 3. At the beginning of the measurement, the membrane was located in dark and the permeance of nitrogen was not observed till 1 h after. And then the membrane was irradiated with UV light, consequently N_2 permeance occurred. After 1 h under light irradiation, the stimulation by light was stopped again. The permeance was observed during ten minutes in dark although the permeance was almost 0. This is due to the vibration of azo derivative on the porous glass surface with the elevated temperature from 298 to 303 K during light irradiation for 1 h.

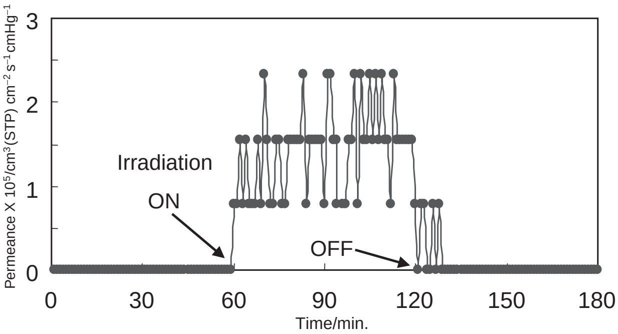


Figure 3. The gas control stability by the surface-modified porous glass membrane in dark and under light irradiation.

Further experiments are now performed for larger permeation and obtaining more fine regulation for several kinds of gases by considering the suitable conditions between the molecular size of azo derivatives and pore size of the substrate.

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