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Light-controlled gas permeability of mesoporous silica glass bearing photochromic spironaphthoxazine on its surface

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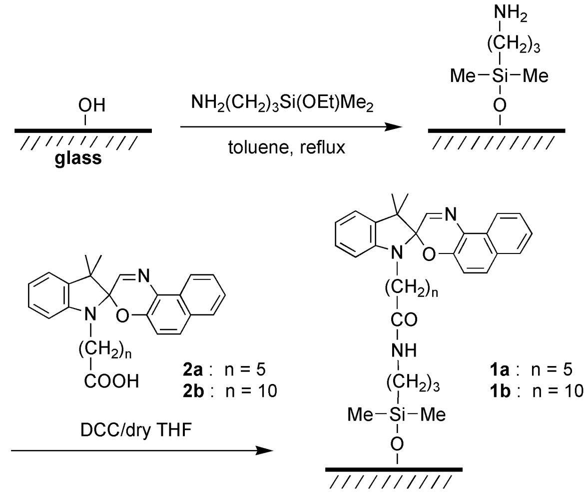
N_2 and CO_2 gas permeability of mesoporous silica glass bearing photochromic indolinospironaphth[2,1-*b*][1,4]oxazine through a covalent linkage was controlled by photo-irradiation: the photo-isomerization of the spironaphthoxazine to the photomerocyanine form suppressed the gas permeation of the glass.

Mesoporous silica glasses have been widely used as platforms for various inorganic–organic hybrid materials such as gas adsorbents,[1] chemical sensors,[2] dye lasers,[3] optical recording media,[4] solid electrolytes,[5] and so on. Their wide applicability is due to the availability of functionalized silica surfaces *via* facile surface modification in addition to the inclusion of guest molecules in their tailored pores.[6] One of the goals of the further development of porous silica materials is the control of their functions by external stimuli such as light. In this regard, gas permeation changes of zeolites, taking advantage of *cis–trans* isomerization of azobenzene adsorped into the zeolitic pores, has recently been studied.[7] However, light-controlled gas permeability of photochromic dye-appended mesoporous silicas obtained by facile surface modification through covalent linkages has scarecely been reported. Here we report the preparation of mesoporous silica glasses bearing photochromic indolinospironaphthoxazine through alkylamide linkages and the control of gas permeability by photo-irradiation.

Indolinospironaphth[2,1-*b*][1,4]oxazine was chosen as the photochromic dye to be appended onto the glass surface because the drastic change in electronic structure resulting after photo-isomerization from a spironaphthoxazine to a photomerocyanine form was expected to perturb the gas permeation of the silica glass. The preparation of the photochromic dye-appended glass is shown in Scheme 1. Tubular or plate mesoporous silica samples (mean pore size 4 nm) were treated with 3-amino-1-ethoxydimethylsilane (20 wt% *versus* the silica glass sample) in toluene at reflux to yield the amino-functionalized silica surface. Then, the spironaphthoxazine moiety was introduced by the condensation of **2a** and **2b**† with the amino group on the silica surface, in the presence of 1,3-dicyclohexylcarbodiimide (DCC), to afford the spironaphthoxazine-appended glass samples **1a** and **1b**, respectively.



Scheme 1

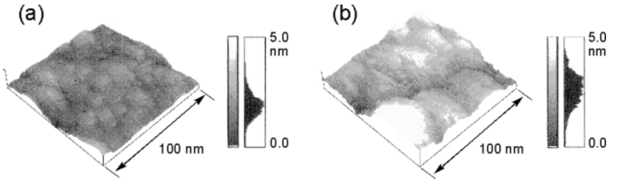


Fig. 1 AFM images and depth distribution of (a) the unmodified mesoporous silica glass and (b) the spironaphthoxazine-appended silica glass **1a**.

Introduction of the spironaphthoxazine onto the glass surface was clarified by AFM analysis as well as MALDI-TOF mass spectroscopy. The AFM images presented in Fig. 1 clearly show that the swell of the surface of the spironaphthoxazine-appended glass increased compared to that of the unmodified glass. This result shows that much of the spironaphthoxazine is distributed on the external surfaces of the silica glass, and some should spread onto the edges and interior surfaces of the mesopores to perturb gas permeability as shown below, although, at this point, it is difficult to investigate the internal part of the mesopores. In the MALDI-TOF mass spectra shown in Fig. 2, the parent peak at *m*/*z* 498 (M^+ for **2b**) was obtained from a chloroform suspension of the well-crushed **2b**-doped silica glass, whereas the chloroform suspensions of the crushed glasses **1a** and **1b** did not afford any peaks around the mass of the spironaphthoxazine moiety. Therefore, it is clear that the spironaphthoxazine moieties in glasses **1a** and **1b** were covalently attached onto the glass surfaces.

In Fig. 3 is shown the electronic absorption spectral changes of **1a** upon photo-irradiation with $\lambda < 330$ nm light. Exposure of the colorless glass **1a** to the light gave rise to a color change

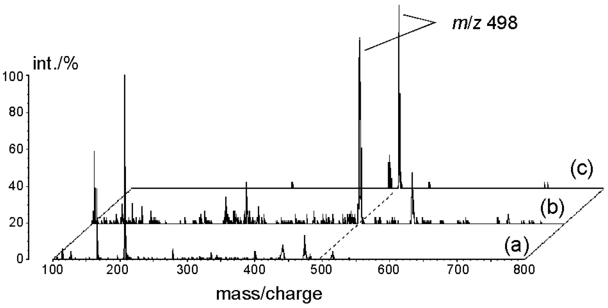


Fig. 2 MALDI-TOF mass spectra of (a) the crushed sample of the glass **1b**, (b) the crushed sample of the **2b**-doped slica glass, and (c) the spironaphthoxazine **2b**. The crushed glass samples were mounted as $CHCl_3$ suspensions.

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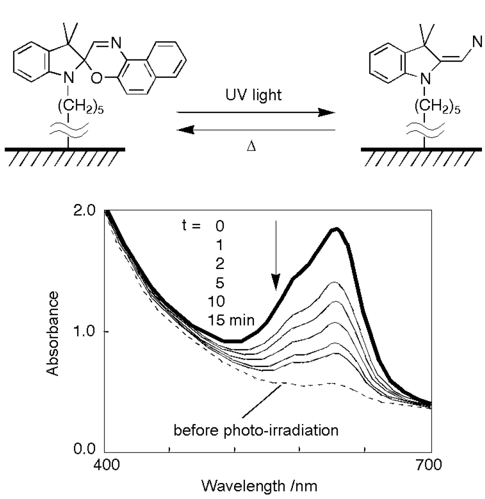

Fig. 3 Electronic absorption spectral changes of glass sample **1a** after 3 min photo-irradiation with < 330 nm light.

to blue: the emergence of the absorption band at 620 nm indicated photo-isomerization from the spironaphthoxazine to the photomerocyanine form. When the irradiation stopped, the absorbance at 620 nm gradually decreased, and the color of the glass was bleached. Thus, the spironaphthoxazine moiety appended onto the glass surface showed positive photochromism in which the photomerocyanine form thermally isomerized to the oiginal structure. A similar photochromic property was observed for glass **1b**. In terms of the fatigue resistance for photo-isomerization, it took 20 repetitions of the photo-irradiation for the absorbance at 620 nm to decrease to 50% of the original spectra in both of the glasses **1a** and **1b**.

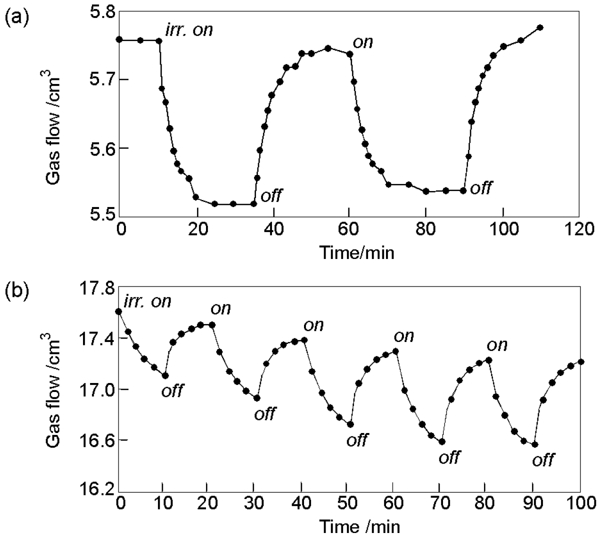

Fig. 4 Time-course profiles of the gas permeability of silica glass **1b** controlled by exposure to the light (1kW Xe lamp); (a) N_2 gas permeability changes, and (b) CO_2 gas permeability upon 10 min photo-irradiation at 10 min intervals. All the experimental processes were carried out under darkness except for photo-irradiation. The labels '*irr. on*' and '*off*' mean the start and end of photo-irradiation, respectively. The gas pressures introduced into the sample compartment were 0.5 and 0.2 kgf cm^{-2} for N_2 and CO_2, respectively.

Light-controlled gas permeability of the spironaphthoxazine-appended glass was investigated using N_2 and CO_2 gasses. In both cases, irradiation of glass **1b** with a Xe lamp (1 kW) gave rise to gas permeability changes of *ca*. 4% (Fig. 4, a and b): the photo-irradiation led to a decrease in gas permeability, and then, the original permeability was reproduced under darkness. As the time-course profile of permeability restoration validly corresponded to the thermal decoloration profile of the colored glass, the control of the gas permeability was based on the photo-isomerization of the spironaphthoxazine appended onto the glass surface. On the other hand, little change in gas permeability was observed for **1a** upon photo-irradiation. Thus, the length of the alkyl linker significantly affected the gas permeability: indeed, the difference in the length of the alkylamide linkers between **1a** and **1b** (*ca.* 6.3 Å)[8] corresponds to 16% of the mean diameter of the pore.

In summary, we have achieved the photo-irradiation control of gas permeation of mesoporous silica by covalently attaching a photochromic indolinospironaphthoxazine onto the surface. The facile preparation of the dye-attached silica surface as demonstrated here is applicable to modified silica glasses with a variety of functional dyes, and therefore, further development of the fine control of silica materials by external optical stimuli will be possible.

Notes and references

† Selected data for **2a** and **2b**: **2a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.20–1.38 (m, 8H), 1.50–1.72 (m, 4H), 2.29 (t, J = 7.3 Hz, 2H), 3.14–3.21 (m, 2H), 6.57 (d, J = 7.6 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 8.9 Hz, 1H), 7.71–7.75 (m, 2H), 8.52 (d, J = 8.9 Hz, 1H); FAB-MS (3-nitrobenzylalcohol) *m*/*z* 428 (M^+). **2b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.03 (s, 3H), 1.20–1.34 (m, 17H), 1.52–1.60 (m, 2H), 2.31 (t, J = 7.3 Hz, 2H), 3.00–3.11 (m, 1H), 3.49–3.60 (m, 1H), 4.82 (s, 1H), 6.60 (d, J = 7.3 Hz, 1H), 6.89 (t, J = 7.3 Hz, 1H), 7.03 (dd, J = 1.3 and 7.3 Hz, 1H), 7.16 (dt, J = 1.3 and 7.3 Hz, 1H), 7.56 (dt, J = 1.3 and 7.3 Hz, 1H), 7.64–7.80 (m, 4H), 7.96 (d, J = 8.2 Hz, 1H), 8.55 (d, J = 8.2 Hz, 1H); FAB-MS (3-nitrobenzylalcohol) *m*/*z* 498 (M^+).

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