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Preparation of Anisotropic Mesoporous Glass and Measurement of Anisotropy in Diffusion by Traveling Chemical Waves

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SUMMARY: Anisotropic mesoporous glass of 30 nm pore diameter was prepared by stretching the softened borosilicate glass along the z-axis before phase separation (spinodal decomposition) took place. The anisotropy in diffusion was measured from the velocity of the traveling chemical waves of the Belousov-Zhabotinksy reaction that proceeded in the mesoporous glass.

Introduction

The Belousov-Zhabotinsky reaction (BZ reaction) distributed in space is known to provide the most well-studied active media, both oscillatory and excitable, for laboratory experiments [1-4]. The dynamic nature of the BZ reaction is originated from the diffusive coupling of nonlinear chemical reactions. Once the minute active units are coupled each other by lateral diffusion, the excitation caused by a local stimulus starts to propagate with constant velocity over the whole medium as a traveling wave that is often called a "chemical wave." The chemical wave is regarded as a laboratory-mimic of the propagating wave of information in biological active tissues.

Nowadays there is an increasing interest among the researchers of active media in working with gel systems, motivated by their explicit advantages. The merits to use gels for constructing active media in the BZ reaction are summarized as follows [5]:

1) *Catalysts can be immobilized.* Even water-insoluble catalysts can be available. Catalysts are often stabler in gels than in a solution. Catalyst-immobilized gel provides an open system.
2) *Hydrodynamic convection is eliminated, thus simple reaction-diffusion rule holds.*

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3) *A bubble-free system is realized because of physical stiffness of gel.*
4) *Diffusion coefficients of activator and inhibitor are controlled to some extent.*
5) *The shape and geometry is well-defined for the active medium that is made of hard gel.* Mesoporous glass is an ideal hard-gel for this purpose. This nature was used to prepare a chemical diode [6, 7], and a curved surface for measuring the drift of a BZ spiral that the kinematic theory [8, 9] predicts. Contrary, soft-gel has a unique merit that is opposite of the hard-gel:
6) *The shape of soft-gel may change by external stimuli, force and internal chemical reactions.* A typical example was provided as self-oscillating gel[10,11].

In addition, the following merit should be pointed out:

7) *Anisotropic medium can be constructed.*

The present contribution reports both the preparation of anisotropic mesoporous glass by applying mechanical share and the measurement of anisotropy in diffusion by use of traveling chemical waves in the BZ reaction. The idea of inducing anisotropy in mesoporous glass by share stress was originated from our observation of anisotropy in mesoporous capillary glass, but not in commercially available mesoporous slab glass, under optical microscope equipped with polalizers. As for the measurement of anisotropy, we applied our previous procedure to estimate the internal structure (tortuosity) of mesoporous glass by use of the BZ wave [12]. From the velocities of the BZ waves in x- and y-direction, for example, we can obtain the ratio of diffusion coefficients D_x/D_y in a mesoporous glass plate. Thus the traveling BZ waves play a role of dynamic probe that reports *in situ* the averaged information concerning the inner structure of gel medium.

Experimental

Preparation of mesoporous glass: A homogeneous mother-block of glass was obtained from a mixture of SiO_2 (62.5 % in weight), B_2O_3 (27.3 %), NaO_2 (7.2 %) and Al_2O_3 (3.0 %) . A small piece of 10 x 25 x 50 mm (x, y and z axises respectively) cut from the mother-block was heated above 800 C then stretched to become two-times longer along the z axis. This shared-glass was kept at 600 C for 16 h; during this period, phase separation of the glass proceeded (spinodal decomposition). From this phase-separated glass, several thin plates of 0.5 mm in thickness were sliced from the x-y, y-z and y-z planes. These glass plates were treated with an aqueous solution of HCl (0.25 M) for 4 days under refluxing conditions to produce mesoporous channels in the glass (pore size 30 nm, porosity 0.4 –0.6 ml/g). The pore size and porosity of the glass can be controlled by this etching process [13)]. After etching, the plates were washed firstly with pure water then methanol to eliminate the remaining water in the channels before drying. All the same procedures but stretching were applied for preparation of isotropic mesoporous glass plates.

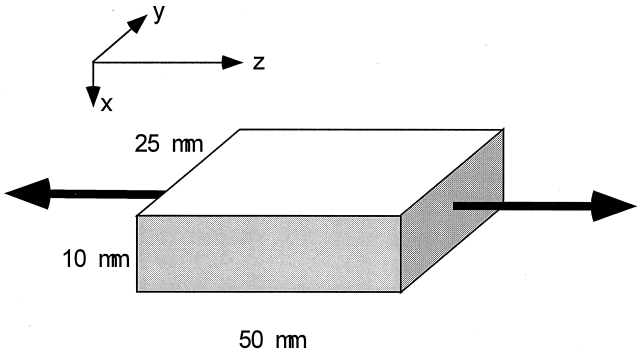

Fig. 1. Stretching the softened borosilicate glass along z-axis before phase separation.

Immobilization of catalyst ferroin: The mesoporous glass plates were soaked in an 80 % methanol solution of ferroin sulfate (5 mM) and dried. This treatment was repeated for 5 times to prepare the ferroin-immobilized mesoporous glass.

Observation of the BZ waves: The ferroin-immobilized mesoporous glass was immersed in the Belousov-Zhabotinsky medium of the following composition: H_2SO_4 (0.235 M), $NaBrO_3$ (0.235 M), malonic acid (0.235 M). All experiments were carried out at room temperature (28 – 30 °C). The chemical waves traveling in the mesoporous glass were monitored under microscope (Wild 8, Leica) with homogeneous blue light (through a band-pass filter of 509 nm) illuminated from the bottom, and recorded on a video recorder (S 11, Mitsubishi) through a B/W CCD camera (XC-77, Sony) connected with video controller (C-2400, Hamamatsu).

Image analysis: The velocity of the BZ waves was calculated from the spatio-temporal diagram of one-line image constructed on a personal computer (NEC PC-9801 VX) equipped with an image-aquisition board (MT-9801-FMM, Microtechnica). The sampling frequency from the video image was 5 Hz or 2.5 Hz. The spatial resolution was 0.02 mm/pixel, and the time resolution was 1/30 s.

Results and Discussion

The BZ patterns observed in the isotropic mesoporous glass were regular concentric waves or regular Archimedian spirals, whereas elliptic waves or distorted spirals in anisotropic mesoporous glass (see Fig.2). This distortion is caused by the difference of velocity of the chemical waves in orthogonal directions, and the difference in velocities reflects the difference in diffusion coefficients. It is well known[12,14)] that the velocity of the BZ waves is proportional to the square root of the diffusion coefficient of autocatalytic species $HBrO_2$:

$$v \sim (D_{HBrO2} k_5 [H^+][BrO_3^-])^{1/2},$$

where D_{HBrO2} is the apparent diffusion coefficient, and k_5 is the rate constants of the autocatalytic reaction in the BZ reaction. Assuming the concentrations of proton and bromate are homogeneous in every direction within the narrow channels of the mesoporous glass, we obtain the ratio of the diffusion coefficients in two orthogonal directions of a single plate from the velocity of traveling BZ waves.

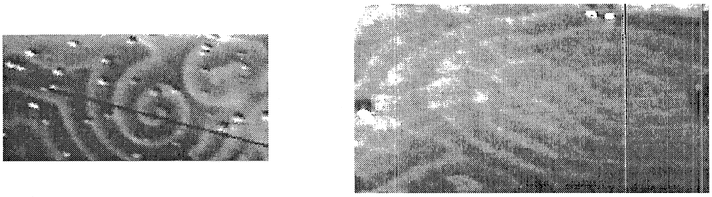

Fig. 2. Morphology of the BZ patterns in 4 I-YZ (left) and in 1A-YZ (right).

We obtained a large anisotropy in diffusion by simple stretching method, as summarized in Table 1. The largest anisotropy was observed in the plate 1A-YZ, where the diffusion coefficient in z-direction was 5.2 times larger than that in y-direction.

As the samples 2A-YZ, 3A-XY and 4 I-YZ had the same pore size and porosity, we may compare these experimental results, though carried out in different sample plates, to get clear insight. Let the velocity of the BZ waves in isotropic glass (4 I-YZ) be 0.031; it is the average of the velocities in two directions. Then we can conclude that the diffusion coefficient of

Table 1. Velocity of the BZ waves and anisotropy of diffusion in mesoporous glass.

Sample	Sliced plane	Pore size	Porosity	Velocity of BZ wave			Anisotropy in diffusion	
		nm	ml/g	v_x	v_y	v_z	D_y/D_x	D_z/D_y
				mm/s	mm/s	mm/s		
1A-YZ	y-z	30	0.6	-	0.022	0.050	-	5.2
2A-YZ	y-z	30	0.4	-	0.031	0.042	-	1.8
3A-XY	x-y	30	0.4	0.023	0.035	-	2.3	-
4 I-YZ	y-z	30	0.4	-	0.029	0.033	-	1.3
5 I-YZ	y-z	30	0.1	-	0.027	0.029	-	1.1

mesoporous glass was changed by the factor of 0.55, 1.0-1.3 and 1.8 in x-, y- and z-direction, respectively, by simple stretching. Roughly speaking, the diffusion coefficient became twice larger than that in isotropic glass. In the x-y plane perpendicular to the direction of stretching, the diffusion coefficient in x-direction became one-half, and no change in y-direction. This result makes sense, because the expansion by stretching along the z-axis must simultaneously cause the compression in x- or in y-direction, or both, depending on the aspect ratio of the glass to be stretched. In the present experiment, mechanical expansion of glass in the z-axis seems to be compensated almost completely by the shrinkage in the x-direction alone, suggesting that the aspect ratio of 2.5 is sufficient to keep one of the axis (y-axis) free from distortion.

Conclusion

The BZ reaction can be a simple and practical tool for measuring the anisotropy in diffusion in porous materials. By this procedure, we have indicated clearly that the anisotropy in diffusion can be induced by stretching the borosilicate glass before phase separation.

On the other hand, the present study raises an interesting question about the origin of anisotropy, or in other words, the symmetry breaking in space. We consider at present the induced anisotropy in diffusion reflects the anisotropy of spatial orientation of mesoporous channels within the glass. It is not clear, however, if this anisotropy is induced during or after the so-called nucleation process. We therefore plan to proceed careful study to understand this mechanism for better control of anisotropic nanostructures in mesoporous materials.

References

1. I.R. Epstein, J.A. Pojman, *An Introduction to Nonlinear Chemical Dynamics*, Oxford Univ. Press, New York – Oxford, 1998.
2. H. Miike, Y. Mori and T. Yamaguchi, *Science of Nonlinear Systems, III, Dynamics in Reaction-Diffusion Systems*, Kodansha Scientific, Tokyo 1997 (in Japanese).
3. S.K. Scott, *Oscillations, waves, and chaos in chemical kinetics,* Oxford University Press, NY 1994.
4. R.J. Field and M. Burger (eds), *Oscillations and traveling waves in chemical systems*, John Wiley & Sons, NY 1985.
5. T. Yamaguchi, L. Kuhnert, Zs. Nagy-Unvgarai, S.C. Mueller, B. Hess, *J. Phys. Chem.* **95**, 5831 (1991).
6. K. Agladze, R.R. Aliev, T. Yamaguchi, K. Yoshikawa, *J. Phys. Chem.* **100**, 13897 (1996).
7. T. Kusumi, T. Yamaguchi, R.R. Aliev, T. Amemiya, T. Ohmori, H. Hashimoto, K. Yoshikawa, *Chem. Phys. Lett.* **271**, 355 (1997).
8. V.A. Davydov, V.S. Zykov, A.S. Mikhailov, *Sov.Phys. Usp.* **34,** 665 (1991).
9. A.S. Mikhailov, V.A. Davydov, V.S. Zykov, *Physica D* **70,** 1 (1994).
10. R. Yoshida, T. Takahashi, T. Yamaguchi, H. Ichijo, *J. Am. Chem. Soc.* **118**, 5134 (1996).
11. R. Yoshida, E. Kokufuta, T. Yamaguchi, *Chaos* **9**, 260 (1999).
12. T. Amemiya, M. Nakaiwa, T. Ohmori, T. Yamaguchi, *Physica D* **84,** 1 03(1995).
13. K. Eguchi, *Studies on Production and Application of Hign Silica Glass*, Reports of the Government Industrial Research Institute, Osaka, 355 (1979).
14. R.J. Field, R.M. Noyes, *J. Am. Chem. Soc.* **96**, 2001 (1974).