Effects of a High Magnetic Field on the Growth of 3-Dimensional Silver Dendrites

Akio Katsuki,* **Ichiro Uechi,**[1] **and Yoshifumi Tanimoto**[1]

Department of Chemistry, Faculty of Education, Shinshu University, Nishi-Nagano, Nagano 380-8544

[1]Institute for Molecular Science, Myodaiji, Okazaki 444-8585

Received June 9, 2003; E-mail: akatuki@gipnc.shinshu-u.ac.jp

A liquid/solid redox reaction between silver ions and copper metal was investigated under a *vertical* and *inhomogeneous* high magnetic field (maximum field strength: 15 T). The 3-dimensional silver dendrites produced via the reaction were drastically affected by the magnetic field. Black and round dendrites were obtained in the magnetic field, whereas metallic silver crystals were grown under the gray dendrites with no field. The yields of the silver dendrite and the copper ion increased significantly in presence of the magnetic field. The results are interpreted in terms of the magnetic convection of the solution, which is induced by the magnetic force on the paramagnetic copper ions generated in the reaction as well as by the Lorentz force on the ions.

The control of a chemical reaction path with a high magnetic field has been an interesting hot topic in chemistry. This is partly because a superconducting magnet, which generates a high magnetic field, is now commercially available, and also because new phenomena, which can not be observed in a low magnetic field, emerge in the high magnetic field. Research on spin control of intermediates or radical pairs by a magnetic field has been widely carried out.[1] The control of crystal orientation by the high magnetic field has been investigated.[2–9] Moreover, our group has found that typical redox reactions show drastic changes under a high magnetic field.[2,10–12] These reports strongly suggest that a high magnetic field is a very useful tool in controlling chemical and physical processes.

Mogi et al. reported various 2D-patterns of silver dendrites in a *vertical* and *homogeneous* magnetic field. Significant changes induced by the magnetic field were interpreted in terms of the magnetohydrodynamic mechanism in which the Lorentz force affects the motions of ions in the magnetic field.[13] We have studied the effects of a *horizontal* and *inhomogeneous* magnetic field on the 2D-pattern and yield of silver dendrites and showed that magnetic forces lead to remarkable effects.[10,11] In a *vertical* and *inhomogeneous* magnetic field, the natural convection due to earth's gravity would be significantly affected by the magnetic force, which is parallel or anti-parallel to gravity and, therefore, a reaction would be influenced.

In this paper, we studied a liquid/solid redox reaction, i.e., the reaction between silver ions and copper metal, under a *vertical* and *inhomogeneous* high magnetic field in order to clarify how *vertical* magnetic forces affect the growth, 3D-pattern, and chemical yield of silver dendrites.[2] It was demonstrated that the *vertical* magnetic forces significantly affect the morphology and chemical yield of silver dendrites. These magnetic field effects are interpreted in terms of the magnetic force and Lorentz force. The magnetic force on paramagnetic copper ions generated via the reaction as well as the Lorentz force on the ions in solution induced convection in the solution, resulting in the ac-

celeration of the reaction rate as well as morphological changes.

Experimental

A superconducting magnet (Japan Superconductor Technology, JMTD-LH15T40) was used in our experiment. It has a room temperature bore tube with a diameter of 40 mm. The distribution of the magnetic field is given in Fig. 1. The maximum field (B) and field (B) × gradient field (dB/dz) were 15 T and 1500 T^2/m, respectively, where z is the distance from the center of the bore tube along the tube. Silver nitrate (Nacalai Tesque GR grade) was used as received. Distilled water was used as the solvent. A copper metal wire (Nilaco, 6ϕ, 99.99%) was polished just before the experiment. The silver nitrate solution (0.05 mol/L) was filled in a cylindrical vessel ($30\phi \times 52$ mm, ca. 34 mL). The vessel was capped with a rubber stopper on which a copper wire (10 mm length) was fixed. Three vessels were placed at the positions in the bore tube, of which B and BdB/dz were 5.6 T and -940 T^2/m for the top position, 15.0 T and $+50$ T^2/m for the middle position, and 9.8 T and $+1070$ T^2/m for the bottom position, as shown in Fig. 1, and one was placed outside of the tube as a control (leak field ca. 0.5 mT). Hereafter, we shall call these positions top, middle, bottom, and outside, respectively. All reactions were carried out at room temperature. After the reaction, the silver dendrite was carefully scratched off the copper wire, washed using distilled water, and dried out at room temperature. The yield of the silver dendrite was measured by gravimetry. The concentration of copper ions was determined from the absorption spectrum of tetraamminecopper(II) complex (the molar extinction coefficient of the complex was estimated as 55.6 at 613 nm) using a HITACHI U-2000 spectrophotometer.

Results

The liquid/solid redox reaction investigated is given by the following equation:
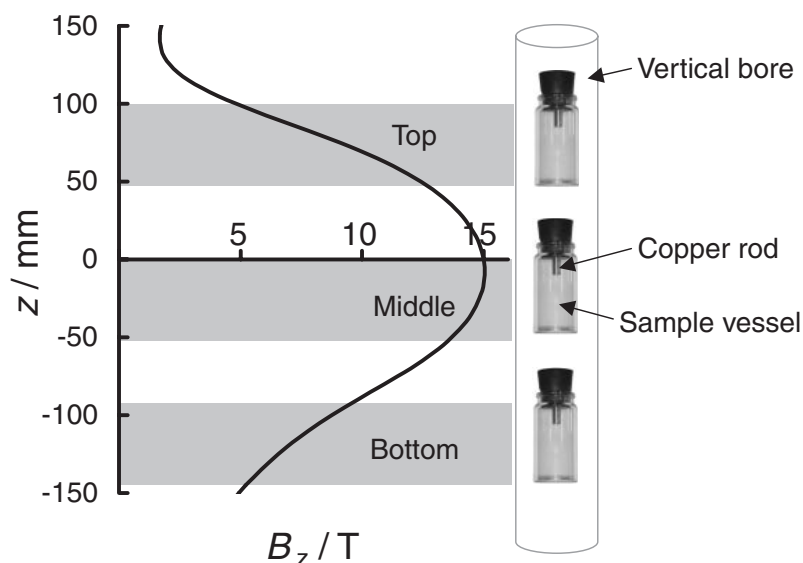
$$2Ag^+ + Cu \rightarrow 2Ag\downarrow + Cu^{2+} \tag{1}$$
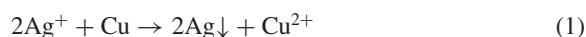
Fig. 1.   The distribution of the vertical magnetic field *B*(*z*). *z* is the distance from the center of the magnetic field (15 T) along the magnetic axis. The gray parts show the area of the magnetic fields where the sample vessels were placed. These positions shall be called top, middle, and bottom from the top. The right-hand vertical bore's picture corresponds to the plot of distribution of the magnetic field.
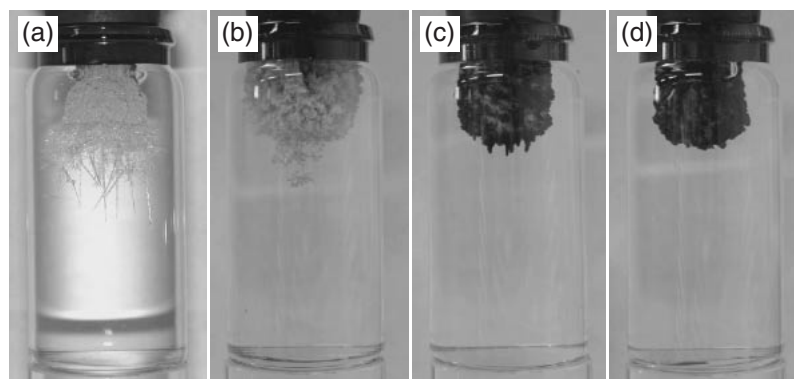

Fig. 2.   The photographs of the silver dendrites after 2 h reaction. (a) the outside of the bore tube (the control < 0.0005 T), (b) the bottom position (9.8 T, $+1070$ T^2/m), (c) the middle position (15.0 T, $+50$ T^2/m), (d) the top position (5.6 T, -940 T^2/m).

The reaction occurs via the ionization potential of copper and silver metal deposits around the copper wire as a dendrite.

Figure 2 shows the photographs of the silver dendrites which grew with and without the magnetic field. The shape and color of the silver dendrites were remarkably affected by the magnetic field. In the control experiment, metallic and bright crystals with tree-like shape were observed under the gray and bulky dendrite. The dendrites that grew under the magnetic field became almost round in shape and dark gray or black in color. The microphotographs shown in Fig. 3 indicate that dendrites generated under the magnetic field have a shape similar to those at zero field, though their size is about 10 times smaller than that grown at zero field. The dendrites grown at the top also contained many small black particles.

Table 1 shows the relative yield of the silver dendrites and the relative concentration of the copper ion after a 2 hour reaction at each position. Both values demonstrate a similar magnetic field dependence. The values in the magnetic field were larger than those on the outside. Both the silver and copper

ion yields at the top position were larger than those at the bottom position, though the magnetic field intensity at the bottom position was about two times larger than that at the top position.

The time evolution of the copper ion yield at each position is shown in Fig. 4. Every value in the magnetic field rose quickly as compared with the value on the outside. For reaction times under 20 minutes, the yield at the middle position increased faster than those at the other positions. When the reaction time exceeded 20 minutes, the yield at the top position was the largest one, and the yield of the middle position was smaller than that at the bottom position.

After a 180-min reaction, about 86, 66, 75, and 44% of Ag$^+$ ion in the solution was deposited at the top, middle, bottom, and outside positions, respectively, and the total amount of Ag$^+$ in the solution was 0.0017 mol. The apparent saturation in copper ion yield observed in magnetic fields is attributable to the decrease in the Ag$^+$ ion concentration with time.

In order to analyze the results semi-quantitatively, the time dependence of the yields was fitted tentatively with a single ex-
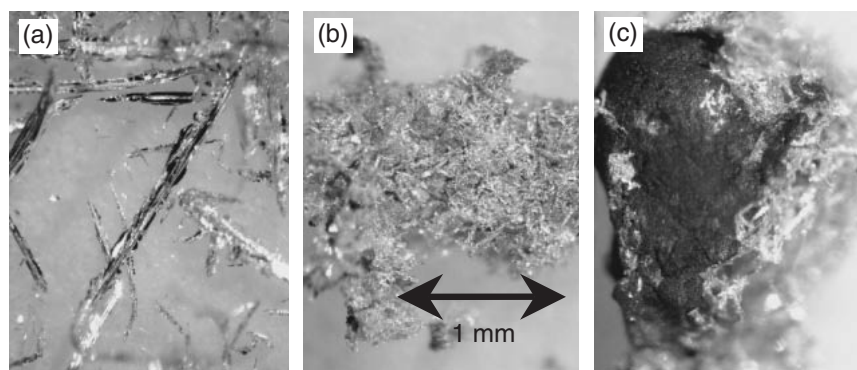
Fig. 3. The microphotographs of the silver dendrites after 2 h reaction. (a) the outside of the bore tube (the control), (b) the bottom position (9.3 T, 980 T^2/m), (c) the top position (5.6 T, -940 T^2/m). The values of the magnetic field strength and magnetic gradient force in (b) and (c) show different values slightly because of the slight different positions.

Table 1. The Effects of the Magnetic Field on the Relative Yields of Copper Ion and Silver Dendrites

	$B/T^{a)}$	Magnetic force[a) /$T^2 m^{-1}$	Ratio[b) Ag	Cu^{2+}
Outside	~0	~0	1.00	1.00
Bottom	9.3	980	1.29	1.54
Middle	15.0	-160	2.08	2.29
Top	5.6	-940	2.06	2.12

a) The values of the magnetic field strength and magnetic gradient force show different values slightly because of the slight different positions. b) The values are the ratio of the yield in the magnetic field and that of the control. These data contain the error of about 10%.
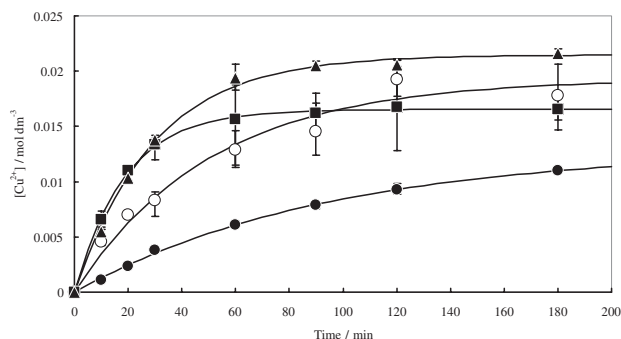
Table 2. Kinetic Rate Parameters of the Copper Ion

	B/T	Magnetic force /$T^2 m^{-1}$	Rate ratio[a)	$Y(\infty)$ /$mol\,dm^{-3}$
Outside	~0	~0	1.00	0.013
Bottom	9.8	$+1070$	1.85	0.019
Middle	15.0	$+50$	5.01	0.017
Top	5.6	-940	3.18	0.021

a) The values are the ratio of the yield in the magnetic field and that of the control.

Discussion

The magnetic field caused obvious changes in the shape and color of the silver dendrites (Fig. 2). The yield of the silver dendrites and the copper ion concentration show similar changes in the magnetic field dependence (Table 1). This fact suggests the copper ion is produced through the reaction (1) quantitatively, with no side reactions in the system.[14] Although the color of the dendrites in the magnet is different from those on the outside, pure silver metal dendrites are generated. The microphotographs (Fig. 3) show that many small-size dendrites appear in the magnetic field. The dendrites grown in magnetic fields are black or dark gray in color, as the incident light will be reflected many times by the small-size dendrites.

In a reaction occurring at the interface of heterogeneous phases like the present one, the rate of a reaction is frequently not controlled by the rate of the reaction at the interface, but by the rate of the transportation of reactants and products to and from the reaction zone. Although diffusion is usually an important process for mass transportation, convection is sometimes a much more important one from a practical point of view. When the temperature of the solution is uniform, natural convection is induced by the difference in the density of solutes, as the gravitational force on each solute is different.

In the present experimental conditions, silver ions in the bulk solution are supplied to the reaction zone, i.e., the surfaces of the copper wire and the dendrites, by convection as well as diffusion. Since the atomic weights of Ag and Cu are 107.9 and 63.55, and since the molar ratio of Ag$^+$ to Cu^{2+} is 2:1 in the redox reaction, the density of the solution containing Ag$^+$ will be higher than that containing Cu^{2+}. This fact indicates that a solution rich in Cu^{2+} moves upward at zero field due to gravity,

Fig. 4. The time evolution of the copper ion concentration: (●) the outsides (the control < 0.0005 T); (○) the bottom (9.8 T, $+1070$ T^2/m); (■) the middle (15.0 T, $+50$ T^2/m); (▲) the top (5.6 T, -940 T^2/m); the solid lines, simulations based on a single exponential function (Eq. 2).

ponential function (2), though this reaction was not the first-order reaction;

$$Y(t) = Y(\infty)(1 - \exp(-kt)) \qquad (2)$$

where $Y(t)$ and $Y(\infty)$ are the yields of Cu^{2+} at time t and infinite, respectively, and k is the rate constant. The fitting results are described in Fig. 4 as solid lines, and the ratios of the rate constants in the magnetic field, at zero field, and $Y(\infty)$ are listed in Table 2. It is clear that the reaction is accelerated by the magnetic field.
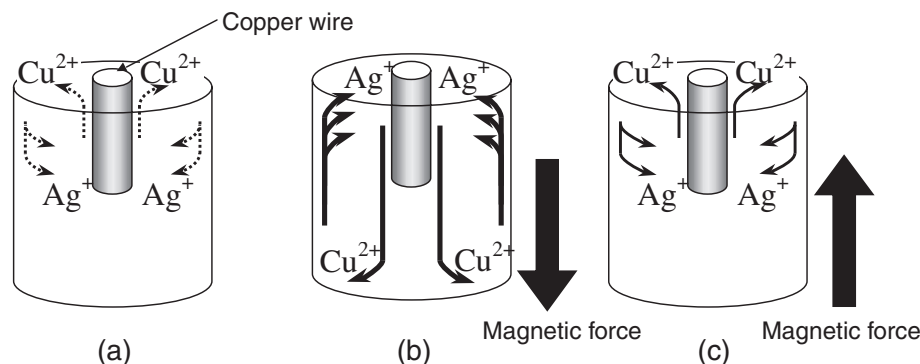
Fig. 5.   The possible mechanism of the magnetic field effect. (a) the outside; the convection caused by gravity, (b) the top (or middle) and (c) the bottom; the convection caused by the magnetic force mainly.

leading to the natural convection of the solution localized within the upper part of the solution in the vessel, as schematically shown in Fig. 5(a). This was confirmed visually by the fact that only the upper part of the solution in the vessel turned light blue after the reaction. The lower part did not react within the observed time duration. This is why $Y(\infty)$ at zero field is about one half of that in magnetic fields (Table 2).

In the presence of a magnetic field, the Lorentz and magnetic forces on solutes and the solvent also induce convection in the solution. The Lorentz force (F_L) and magnetic force (F_M) are given by the following equations,

$$F_L = ev \times B \qquad (3)$$

and

$$F_M = \chi \frac{1}{\mu_0} \frac{dB(z)}{dz} B(z) \qquad (4)$$

where e is the electric charge of an ion, v is its velocity, B is the magnetic field, χ is the molar magnetic susceptibility, and $dB(z)/dz$ is the magnetic field gradient at the position z apart from the center of the magnetic field along the bore. Molar magnetic susceptibilities of copper metal, copper ion, silver, and silver ion are $-4\pi \times 5.46 \times 10^{-12}$ m^3 mol^{-1}, $+4\pi \times 1.28 \times 10^{-9}$ m^3 mol^{-1}, $-4\pi \times 2.05 \times 10^{-11}$ m^3 mol^{-1}, and $-4\pi \times 2.4 \times 10^{-11}$ m^3 mol^{-1}, respectively. The F_L works in the direction which is vertical to both v and B. The motion of ions in the horizontal plane is accelerated by F_L. On the other hand, F_M works along the direction of B, and attracts or repels ions and molecules in the vertical direction. In a high magnetic field, the F_M on a paramagnetic ion becomes strong enough to induce convection. At the top and bottom positions the forces on the copper ions are estimated at -12.0 N/mol and $+13.7$ N/mol, respectively, whereas those on the silver ions are estimated at -0.23 N/mol and $+0.26$ N/mol, respectively. The magnetic force on the copper ions is strong enough to induce convection in a solution, since it is about 19 times larger than gravity. The estimation of the Lorentz force on thermally moving ions in solution is very difficult, though it is easy for ions moving in a vacuum. Ions in a solution are solvated by water, and their mass and size are unknown. Solute–solvent and solute–solute interactions affect the velocity of ions. The velocity of ions moving in a solution is unclear, even though it is plausible that the Lorentz force appreciably affects the motion of ions in solution, as previously reported.[13,15,16] Therefore, it is

reasonable to think that both the Lorentz force and magnetic force contribute in our interpretation of the present magnetic field effects.

The area of highest yield of Cu^{2+} ion is in the order of middle $\cong$ top > bottom up to 20 minutes after the reaction starts, and then changes to top > bottom > middle (Fig. 4). On the other hand, B and $|BdB/dz|$ are in order of middle > bottom > top and bottom $\cong$ top > middle, respectively. The magnetic field dependence of the yield does not match well with the magnetic field strength nor the magnetic field gradient strength. The observed effects can not be explained solely by the Lorentz force nor the magnetic force. They are explained by the combination of both forces, as discussed below.

In the early reaction stages, where the concentration of the copper ion is low, the force due to Eq. 3 would dominate in the reaction system. Therefore, before a reaction time of 20 minutes, the copper ion concentration at the middle position (15 T, -160 T^2 m^{-1}) grew faster (Fig. 4) and the simulated reaction rate was larger (Table 2) than those at the other positions. The motion of silver ions is accelerated by the Lorentz force. This causes an increase in the frequency of the collisions between the silver ions and the copper metal surface. As a result, the efficiency of the redox reaction is improved. Most of the reaction duration, however, is driven predominantly by the magnetic force in Eq. 4, primarily because the copper ion concentration at the middle position is lower than that at the bottom position (9.3 T, 980 T^2 m^{-1}) at 180 min, and, secondly, the yield of the silver dendrite at the top position (5.6 T, -940 T^2 m^{-1}) is larger than that at the bottom position, even though the magnetic field strength at the bottom position is stronger than that at the top position. The appearance of the copper ion causes a major change in the magnetic field. Accordingly, the Lorentz force does not significantly contribute to the observed results. This is because the direction of convection due to the magnetic force is vertical, which is suitable for removing Cu^{2+} from the reaction zone and, as a result, for supplying fresh solution from the lower part of the vessel to the reaction zone, whereas the Lorentz force induces convection of the solution only in the horizontal plane.

We can explain the dense structure of the dendrite in the magnetic field roughly as follows: At the top (and the middle[17]) position (Fig. 5(b)), the magnetic forces on the copper ions around the copper wire are downward. As the copper ion rich solution around the copper wire moves out by the magnetic

forces, a fresh bulk solution, which is rich in silver ions, is supplied to the surface of the copper wire. All of the solution in the vessel undergoes the magnetic convection. As a result, the redox reaction (1) is promoted effectively, and the yield accelerated about double that at the present condition. On the other hand, at the bottom position (Fig. 5(c)), the copper ions around the wire receive an upward magnetic force. This means that the convection zone becomes small as compared with that at the top position. Accordingly, the reaction is not accelerated much by the magnetic force.

Now, we move on to the shape of the dendrites in the magnetic field. For the purpose of comparison, the effects of the concentration of Ag^+ on the shape of the dendrites were examined at zero field. At low concentration, the metallic and bright crystals grew like a tree under the gray and bulky dendrites. With increasing concentration, the color of the dendrites changed to black, and no metallic crystals were formed. This means that the morphology of the dendrites is significantly affected by the reaction rate. At low concentration, the reaction rate is slow and the metallic crystals grow slowly after the initial deposition of gray dendrites. At high concentration, the rate is so fast that small particles and dendrites deposit on the copper wire. Therefore, the morphological change induced by the magnetic field is attributable to the acceleration of the reaction rate caused by the magnetic field-induced convection. Black and round dendrites grew in the magnetic field due to the acceleration, whereas tree-like crystals were formed at zero field.

In a previous paper, we have studied the effects of a high *horizontal* magnetic field (8 T, ca. 400 T^2/m) on the 2D-pattern of silver dendrites generated by the redox reaction (1), where the dendrites were deposited on chromatography paper.[10,11] The dendrite shape changed remarkably, and the yield increased by about 50% in the magnetic field.[11] In this experiment, the magnetic field is perpendicular to gravity and, therefore, interference between the magnetic force and the gravitational force is minimum. Furthermore, the Lorentz force does not contribute to the reaction, as the reaction was carried out in the two-dimensional plane. These results were interpreted solely in view of the magnetic force on the copper ion generated by the redox reaction, which caused magnetic convection of the solution and accelerated the redox reaction. This interpretation was further verified by the computer simulation study.[12] In the present experiment, since the reaction was carried out in 3-dimensional space, the influence of the Lorentz force in addition to the magnetic force is also taken into consideration. The morphology of dendrites at zero field would be affected partly by the natural convection and would be further modified by the magnetic force and the Lorentz force in the magnetic field.

Conclusion

The magnetic field dramatically affects the growth behavior, shape, and amount of the silver dendrites. The results are interpreted in terms of the magnetic and Lorentz forces, of which the former contribution would be dominant compared to the latter. This is because the direction of the magnetic force is vertical which is suitable for convection of the whole solution at the

present experimental condition, whereas that of the Lorentz force is horizontal. The magnetic force intensifies or diminishes a gravity force in chemical reaction. These results suggest that magnetic fields are highly useful in controlling redox reactions at the interface between liquid/solid phases.

References

1 "Dynamic Spin Chemistry," ed by S. Nagakura, H. Hayashi, and T. Azumi, Kodansha, Tokyo (1998).

2 A. Katsuki, I. Uechi, M. Fujiwara, and Y. Tanimoto, *Chem. Lett.*, **2002**, 1186.

3 A. Katsuki, R. Tokunaga, S. Watanabe, and Y. Tanimoto, *Chem. Lett.*, **1996**, 607.

4 M. Fujiwara, T. Chidiwa, R. Tokunaga, and Y. Tanimoto, *J. Phys. Chem. B*, **102**, 3417 (1998).

5 M. Fujiwara, R. Tokunaga, and Y. Tanimoto, *J. Phys. Chem. B*, **102**, 5996 (1998).

6 M. Fujiwara, M. Fukui, and Y. Tanimoto, *J. Phys. Chem. B*, **103**, 2627 (1999).

7 Y. Tanimoto, R. Yamaguchi, Y. Kanazawa, and M. Fujiwara, *Bull. Chem. Soc. Jpn.*, **75**, 1133 (2002).

8 J. Torbet, J.-M. Freyssinet, and G. Hudry-Clergeon, *Nature*, **289**, 91 (1981).

9 M. Ataka, E. Katoh, and N. I. Wakayama, *J. Cryst. Growth*, **173**, 592 (1997).

10 A. Katsuki, S. Watanabe, R. Tokunaga, and Y. Tanimoto, *Chem. Lett.*, **1996**, 219.

11 Y. Tanimoto, A. Katsuki, H. Yano, and S. Watanabe, *J. Phys. Chem. A*, **101**, 7359 (1997).

12 W. Duan, M. Fujiwara, and Y. Tanimoto, *Bull. Chem. Soc. Jpn.*, **73**, 2461 (2000).

13 I. Mogi, S. Okubo, and Y. Nakagawa, *J. Phys. Soc. Jpn.*, **60**, 3200 (1991).

14 The initial pH conditon of the solution was neutral. During copper ions were produced by the redox reaction, precipitation such as a copper hydroxide did not appear in our experimental condition.

15 K. Shinohara and R. Aogaki, *Electrochemistry*, **67**, 126 (1999).

16 A. Sugiyama, S. Morisaki, and R. Aogaki, *Mater. Trans., JIM*, **41**, 1019 (2000).

17 The magnetic force at the middle position is much smaller than that at the bottom position. Therefore, vertical convection does not occur effectively at the middle position, though the direction of the convection of the copper ions is downward. In contrast, at the bottom position, the vertical convection occurs, even though the convection volume is small as shown in Fig. 5(c). As a result the yield at the middle position becomes smaller than that at the bottom position.