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Transition from an unstable synchronization state with transient oscillation cessations to spiral rotation in a coupled chemical oscillator system

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Spatiotemporal patterns of chemical wave propagation in the assemblies of nine cation-exchange beads loaded with the catalyst ferroin of Belousov–Zhabotinsky reaction are reported. The beads are immersed in the reaction mixture, on which periodic chemical waves are emerged. In the bead assemblies, abrupt changes of initiation site and direction of the periodic chemical waves were observed. In some cases, it was observed that transient oscillation cessations and the following rotating spiral wave occur. © 1997 American Institute of Physics. [S0021-9606(97)51708-9]

Recently, catalyst-fixed gels have been extensively used to study spatiotemporal patterns exhibited in chemical reactions.^{1–4} Striking studies in this area are the studies^{5–7} by Maselko and Showalter. In their studies, the ferroin catalyst in the Belousov–Zhabotinsky (BZ) reaction was immobilized on cation-exchange beads. They studied the chemical wave patterns on the spherical surface of a single bead and in the thin layers of the beads. With the same experimental system, we have examined the synchronization of three to nine bead assemblies in oscillatory states.^{8,9} It is thought that this experimental system provides useful models for a moderate number of coupled oscillatory or excitable elements, of which data is still lacking due to the many difficulties with experiments. Here, we report the dynamic behaviors of assemblies of nine beads. We observed unstable synchronization states in which the wave initiation bead temporally changes. In some cases, it was observed that the unstable synchronization state with transient oscillation cessations switches abruptly to a stable rotating spiral wave.

Our experimental system is almost the same as that of Maselko and Showalter^{5–7} and described in our earlier reports.^{8,9} Cation-exchange beads (DOWEX, 50W-X2) loaded with the catalyst ferroin were immersed in the BZ solution. The initial concentrations of the BZ reactants were as follows: potassium bromate 0.2 M; malonic acid 0.4 M; sulfuric acid 1.0 M. The initial ferroin amount of the loaded beads was 3.6×10^{-4} mol/g beads. The beads with some manipulation approached each other to form an assembly of nine beads. The positions of nine beads were fixed in an experimental run. Some beads touched and some beads did not touch but were closely located ($< 50 \mu\text{m}$). Chemical wave propagations were observed by an inverted microscope coupled to a CCD video camera and monitored as the change of the transmitted light intensity for some beads in a bead assembly. At the same time, the chemical wave propagations and the corresponding changes of nine beads' color were recorded with a time-lapse video recorder. Measurements were performed at room temperatures ($22 \pm 2^\circ\text{C}$).

Both stable and unstable synchronization states were observed. In the stable synchronization states, the initiation site of chemical waves propagating periodically were fixed to

one bead. The video images for an example of the beads assembly in the unstable synchronization states are shown in Fig. 1. In one synchronization mode [Fig. 1(a)], the initiation site and the direction of periodic chemical waves did not change for about twenty times. However, this mode changed abruptly to another mode [Fig. 1(b)] which then continued

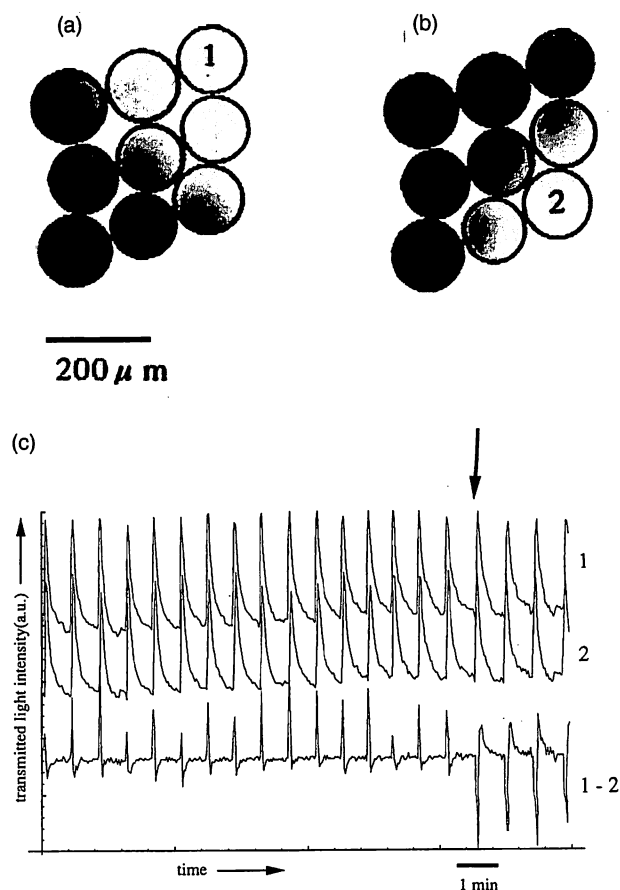


FIG. 1. Abrupt transition from one synchronization mode (a) to another mode (b). In (a), a chemical wave started from bead (1) and propagates over the nine beads assembly and that was repeated. In (b), the initiation site was bead (2). (c) shows the transmitted light intensities and the light intensity difference as a function of time for the two beads [(1) and (2)]. The arrow denotes the transition point.

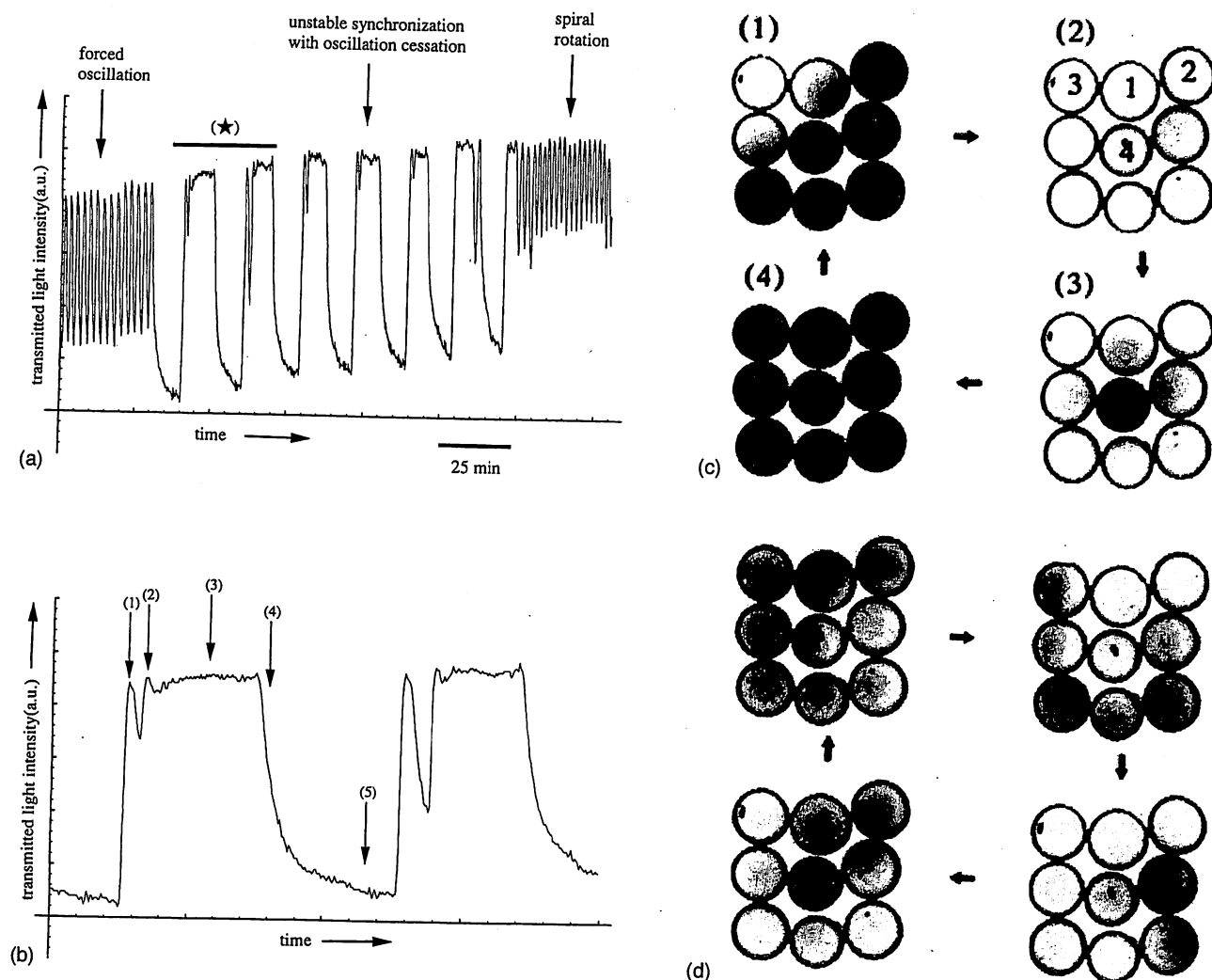


FIG. 2. The transition from the unstable synchronization state with oscillation cessations to spiral wave rotation. (a) Transmitted light intensity as a function of time for a single bead of nine beads assembly in an unstable synchronization state with oscillation cessations. One region (★) of the unstable synchronization state is enlarged and shown in (b). The time points denoted by numbers (1), (3), (4), and (5) corresponds to the images (1), (2), (3), and (4) of (c), respectively. (d) shows spiral wave rotation [see (a)] emerged in the same beads assembly.

for several times at least. Figure 1(c) shows the transmitted light intensities and the light intensity difference as a function of time for two beads (bead1, bead2) in the bead assembly of Figs. 1(a) and 1(b). The arrow denotes the time point of the transition from one synchronization mode [Fig. 1(a)] to another mode [Fig. 1(b)].

In some experimental runs we observed that the unstable synchronization state switched to a stable wave rotation. Figure 2(a) shows transmitted light intensity as a function of time for a single bead [bead (1) in Fig. 2(c)] of a bead assembly exhibiting the switching. The color of beads immersed in the reaction solution was dark blue for an induction time (<2 h). After that, the bead's color changed to be red and periodic chemical wave started to propagate. The induction time for each bead was different. In Fig. 2(a), in the region before the unstable synchronization state with oscillation cessations, a single bead [bead (2) in Fig. 2(c)] which perhaps had longer induction time stayed to be blue and the other eight of nine beads already changed the colors to red. Periodic chemical waves started from the single blue

bead and propagated over the bead assembly. Just after the single blue bead changed the color to red, the unstable synchronization with oscillation cessations emerged. One region [(★) in Fig. 2(a)] in the unstable synchronization state with oscillation cessations is enlarged in Fig. 2(b) and the corresponding video images are shown in Fig. 2(c). One chemical wave [the arrow (1) in Fig. 2(b) and the image (1) in Fig. 2(c)] started from one bead [bead (3) in Fig. 2(c)]. Immediately after that, second wave [the arrow (2) in Fig. 2(b)] started from bead (1) in Fig. 2(c) (the corresponding image not shown). The two sequential chemical waves propagating from different beads resulted in the transient cessations of oscillation in all beads [the arrow (3) in Fig. 2(b) and the image (2) in Fig. 2(c)], which also became shallow blue. It was followed that the central bead [bead (4) in Fig. 2(c)] changed the color to red [the arrow (4) in Fig. 2(b) and the image (3) in Fig. 2(c)] and finally all the beads changed their colors to red [the arrow (5) in Fig. 2(b) and the image (4) in Fig. 2(c)]. This repeated several times. At one point in time during the unstable synchronization state, two chemical

waves started from different beads broke into each other and a stable rotating spiral wave abruptly occurred. Figure 2(d) shows the rotating wave for one period. The direction is counterclockwise.

In the original study with cation-exchange beads by Maselko and Showalter,⁶ it had been reported that a circular wave pattern in the thin film of ferroin loaded cation-exchange beads gradually transits to an irregular pattern with an increasing BrO_3 or H_2SO_4 concentration in the reaction solution. The first irregular pattern with increased concentrations became the target pattern and had a spiral center. Our observation of the transition from the unstable synchronization state to the spiral wave rotation might provide an insight to the origin of the spiral center in the target pattern observed by Maselko and Showalter, although the H_2SO_4 concentration was much higher in our experiments.

We now have no explanations for the complex dynamic behavior as shown in Fig. 2(c). The behavior similar to transient cessations of oscillation in a bead assembly was also observed in our previous study⁹ of three beads distributed in a triangular form not in contact with each other. We observed only the transient cessations of oscillation where all the beads are red and not the state where all the beads are shallow blue. It had been suggested that reversible switching between oscillatory and excitable states of the beads might occur. Our observation of the unstable synchronization state with the transient cessations of oscillations might be inherent in coupled oscillatory and/or excitable elements. In addition,

the H_2SO_4 concentration was very high in our experiments. The high H_2SO_4 concentration results in the ferroin's dissociation from the beads and the decomposition of the ferroin in the reaction solution. Thus, the coupling strength among the beads and the native periods of each beads are thought to change gradually. The unstable synchronization state with the oscillation cessations might be also responsible for the ferroin dissociation and decomposition. The dynamic behavior dependent on the H_2SO_4 concentration in the reaction solution should be pursued further to examine the cause of the unstable synchronization and that study is now in process.

Experimental results [Fig. 1(c) and Figs. 2(a) and 2(b) in the text] were visualized with the software Wolfram Research, *Mathematica*. We thank Mr. Bob Serveter for his careful reading of the manuscript.

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