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Chemical Waves on the Surface of a Photosensitive Monolayer

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Abstract: We report the observation of chemical waves propagating on the surface of a $Ru(bpy)_3^{2+}$ monolayer formed on the Ce^{4+}- and Mn^{2+}-catalyzed Belousov–Zhabotinskii (BZ) reactors. A fraction of $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$ as the catalyst in the reactor changes to its oxidized state in the oscillatory reactions. The amount of $Ru(bpy)_3^{3+}$ produced is too small to be detected by visible absorption measurement, but the use of fluorescence microscopy allows us to visualize the oxidation process as a clear image of oxidized wave formation. The shape of the wave front shows a large sensitivity to illumination with visible light when Ce^{4+} is used as catalyst. Strong illumination even destroys the wave front, creating a pair of rotating spirals.

Introduction

Chemical reactions far from equilibrium in catalytic media may exhibit spatio-temporal structures such as expanding target patterns and rotating spiral waves, as exemplified by the Belousov–Zhabotinskii (BZ) reaction[1] or the CO oxidation on platinum.[2] In case of the BZ reactor, most studies have been performed in homogeneous aqueous solutions, but recently there has been growing attention on the use of gel matrices.[3] Among various gel systems, especially attractive are immobilized-catalyst ones[4,5] in which reaction occurs only at the catalyst surface, producing a rich variety of spatial behavior. We have found previously[6] that $Ru(bpy)_3^{2+}$ monolayers formed on the Ce^{4+}-catalyzed BZ reactor show temporal luminescence oscillations as a result of oscillatory chemical reactions in the subphase. The BZ reactor/monolayer coupled configuration offers a new class of inhomogeneous excitable system where a wealth of interesting self-organization in two dimensions may be expected. Here we report for the first time the evolution of spatial patterns on the monolayer surface of this coupled system. Typical patterns obtained are chemical waves propagating as closed circular waves or spirals. On the Ce^{4+}-catalyzed BZ reactor, the shape of the wave front can be modified by illumination with strong visible light. The wave front is even broken to produce two free ends which develop to form a pair of counter-rotating spirals as commonly observed in the conventional light-sensitive BZ media.[7,8]

Experimental Section

The BZ reactor was prepared from Milli-Q purified water and reagent grade chemicals. The initial concentrations adopted for standard solutions were 0.36 M H_2SO_4, 0.16 M $NaBrO_3$, 0.3 M $CH_2(COOH)_2$, 0.003 M $Ce(NH_4)_2(NO_3)_6$ or $Mn(NO_3)_2$, and 0.1 M $HClO_4$. The reaction solution was stirred until Ce^{4+}–Ce^{3+} oscillations started, and then the solution was poured into a Petri dish (diameter: 8.5 cm) with a layer thickness of 1.2 or 0.5 mm, which was placed on the stage of an Olympus fluorescence microscope.

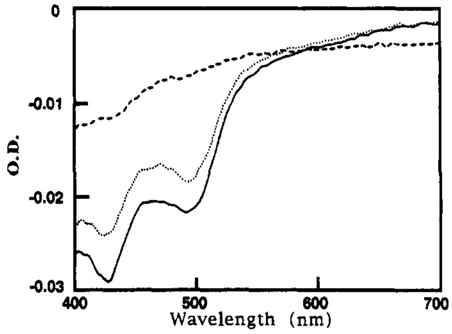

Figure 1. Reflection spectra of $Ru(bpy)_3^{2+}$ monolayers on 0.1 M $HClO_4$ with varying initial concentrations of Ce^{4+}: (—) 0 M; (···) 0.003 M; and (– –) 0.03 M. Occupied area per molecule is about 90 Å². The ordinate represents optical density (O.D.) defined by O.D. = $\log(R_0/R_m)$, where R_m and R_0 denote the reflected light intensities from the surface of the subphase with and without $Ru(bpy)_3^{2+}$ monolayer, respectively.

A surfactant derivative of $Ru(bpy)_3^{2+}$, $(bpy)_2Ru^{II}[bpy(COOC_{18}H_{37})_2]^{2+}(PF_6^-)_2$, was synthesized by a literature method.[9] Monolayers of this compound were spread from chloroform solution onto the reactor surface (occupied area per molecule: ~90 Å²). About 10 min after spreading the monolayer, fluorescence microscope observation was started to detect spatial patterns. The BZ reactor/monolayer coupled system was illuminated by blue exciting light (410–490 nm, peak wavelength: 436 nm) from a 100-W mercury lamp which was focused on the monolayer through an objective (Olympus, MDPlan 5 or 10). The resultant luminescence from the monolayer was separated from the exciting light with a dichroic mirror and viewed with an ICCD camera (Hamamatsu, C3500) and was recorded on videotape. All the experiments were carried out at 26 ± 1 °C. On the luminescence images, oxidized waves appeared dark since the oxidized form $Ru(bpy)_3^{3+}$ was nonluminescent. The waves could be distinguished from reduced background in the absence of ClO_4^-, but the contrast was poor because of weak luminescence from the reduced region. $HClO_4$ was therefore mixed in the reaction solution in order to enhance the luminescence intensity of the $Ru(bpy)_3^{2+}$ monolayer.[6]

Visible reflection spectra of the monolayer were measured by a multichannel spectrophotometer equipped with optical fiber probes (Otsuka Electronics, MCPD-110). The monolayer was illuminated with white light which was guided by an optical fiber from a 150-W halogen lamp, and the signal reflected directly from the monolayer was detected by the same fiber probe.

Results and Discussion

Wave Formation in the BZ Reactor/Monolayer System. In our experiments, oxidized waves are seen to form spontaneously and propagate on the monolayer surface. The spatial pattern is not observed on reactant solutions containing no catalyst,

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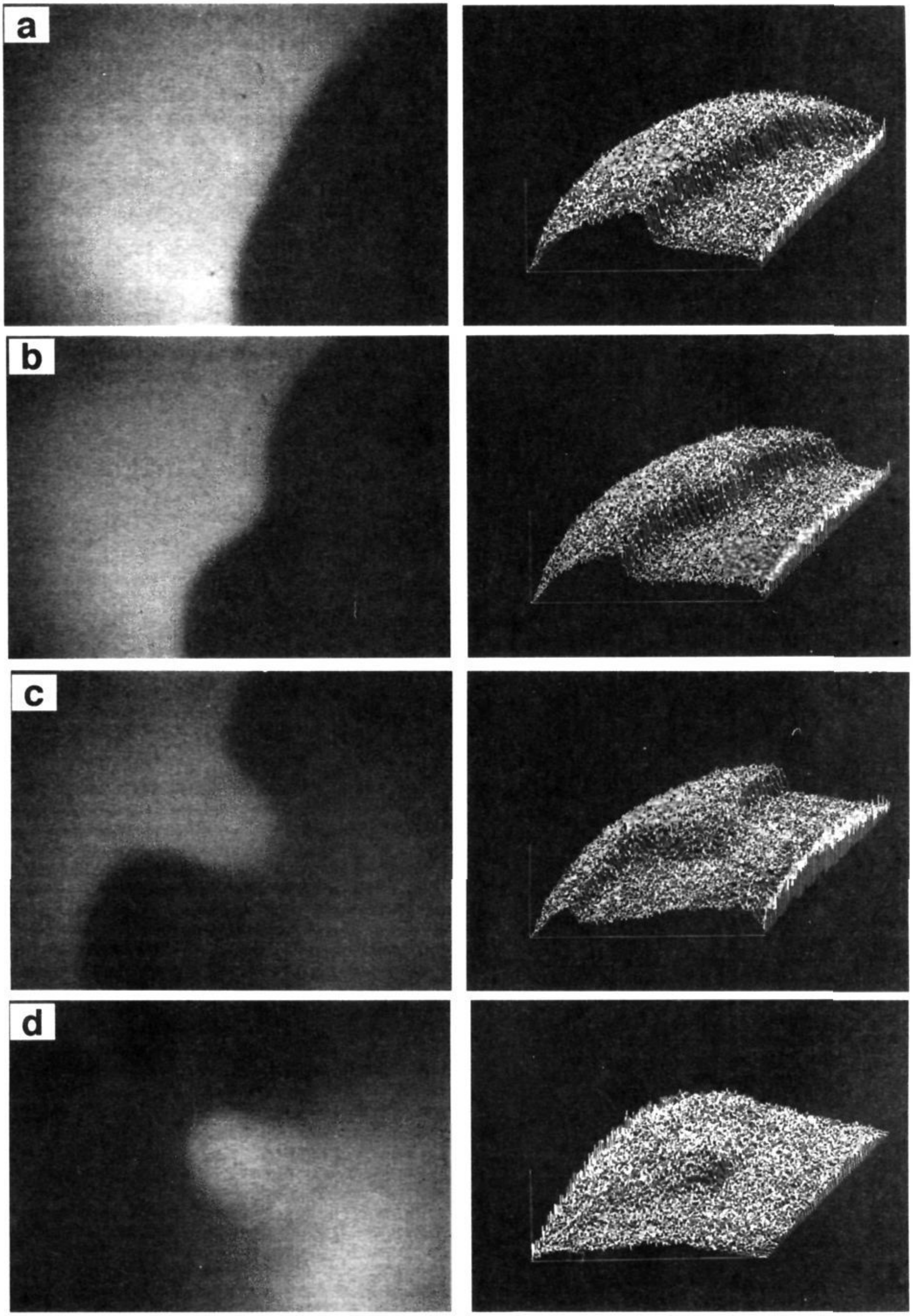

Figure 2. Time evolution of a wave front on the surface of a $Ru(bpy)_3^{2+}$ monolayer formed on a Ce^{4+}-catalyzed BZ reactor and its three-dimensional profile. The exciting light (intensity: 280 mW/cm^2) was focused to a diameter of about 450 μm on the monolayer throughout the experiment. Each micrograph was taken by widening the microscope field in a flash. The three-dimensional profile is a view from the bottom side of the corresponding micrograph, except for d which is viewed from the top side. Image area: 1.65 × 1.23 mm^2. BZ layer thickness: 1.2 mm. Time elapsed between a and d: 10 s.

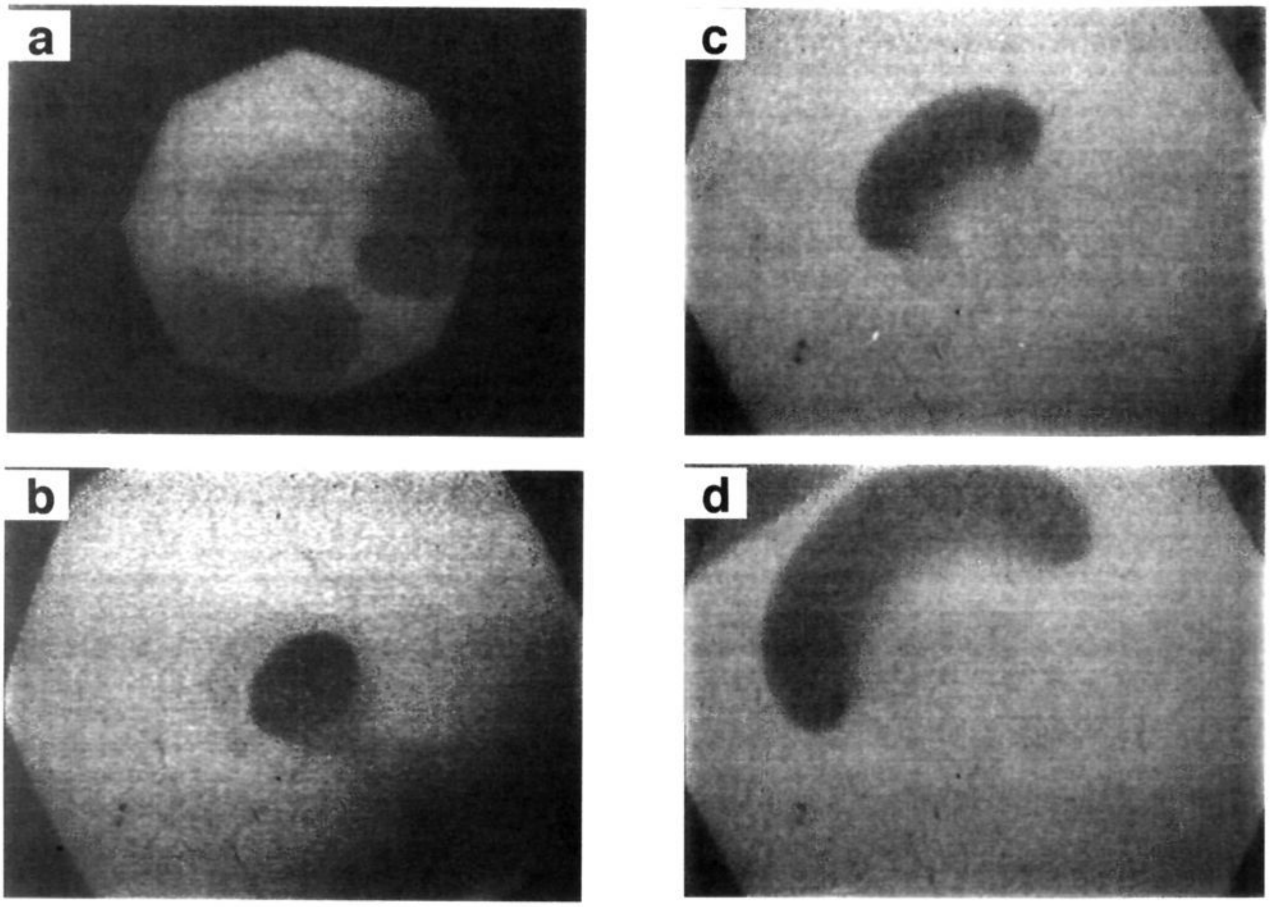

Figure 3. Time evolution of oxidized waves on the surface of a $Ru(bpy)_3^{2+}$ monolayer formed on a Ce^{4+}-catalyzed BZ reactor. The wave front had been broken by focusing the exciting light (intensity: 280 mW/cm^2) to a diameter of about 1 mm on the monolayer, and then the pictures were taken at 9.3-s intervals under continuous illumination with the exciting light (intensity: 68 mW/cm^2). Image area: 3.30 × 2.46 mm^2. BZ layer thickness: 0.52 mm.

suggesting that the wave formation occurs as a consequence of the oxidation of $Ru(bpy)_3^{2+}$ by the oxidized catalyst (Ce^{4+} or Mn^{3+}) in the subphase according to the reaction

$$Ru(bpy)_3^{2+} + cat.^{(n+1)+} \rightarrow Ru(bpy)_3^{3+} + cat.^{n+} \quad (1)$$

The character of wave phenomena in the monolayer is therefore governed to a great extent by the oscillatory behavior of the catalyzed subphase, especially close to the air–water interface. For the monolayer on a 0.5-mm layer solution, we often see the evolution of a regular wave pattern composed of concentric trigger waves and/or rotating spirals. These waves apparently arise from $cat.^{(n+1)+}$ waves that are spontaneously initiated in the subphase around heterogeneous sites such as the wall of the Petri dish, impurities, and gas bubbles. On a 1.2-mm layer solution, the monolayer assumes a rather complex pattern with the regular waves distorted by a number of new wave sources which appear randomly over the whole monolayer surface. Such turbulences are thought to be brought about by some convective motions between the bulk solution and the monolayer-covered surface layer where the excitability is reduced by oxygen.[10,11]

The oxidation of $Ru(bpy)_3^{2+}$ might be also expected to be followed by visible absorption measurement of the monolayer. However, it is found that this is not the case in our system. In Figure 1 we show typical reflection spectra of $Ru(bpy)_3^{2+}$ monolayers spread on 0.1 M $HClO_4$ with varying initial concentrations of Ce^{4+}. Solid and dashed curves can be recognized as representative of $Ru(bpy)_3^{2+}$-rich and $Ru(bpy)_3^{3+}$-rich monolayers, respectively. When the monolayer is formed on the Ce^{4+}-catalyzed BZ reactor, its reflection spectra, monitored each time after thoroughly stirring the reaction solution to assure spatial homogeneity on a scale comparable to the diameter of the fiber probe, are almost identical to the solid curve in Figure 1. Moreover, the spectra exhibit no marked time dependence, while periodic Ce^{4+}–Ce^{3+} oscillations do take place in the subphase. This means that only a small portion of the total $Ru(bpy)_3^{2+}$ is converted to $Ru(bpy)_3^{3+}$ on the BZ reactor, which is difficult to detect within the resolution of the spectrophotometric system. The small $Ru(bpy)_3^{3+}$ concentration is understandable in light of the very low conversion level of the Ce^{4+} system itself in the oscillatory reactions.[12] In addition, the formation of an electric double layer beneath the cationic monolayer plays an equally crucial role in the suppression of reaction 1 by preventing the oxidized catalyst from interacting efficiently with the $Ru(bpy)_3^{2+}$ molecules.

That the amount of $Ru(bpy)_3^{3+}$ remains significantly low even in an oxidized wave may imply the potential difficulty of applying the conventional two-dimensional spectrophotometry[7,8] for the observation of wave propagation. In our experiments, the use of a fluorescence microscope together with a low light level camera enables us to readily detect the faint contrast between oxidized and reduced regions on the monolayer surface as concretely illustrated below. We suspect that the excited state of $Ru(bpy)_3^{2+}$ is quenched effectively by a fraction of $Ru(bpy)_3^{3+}$ present in the monolayer, and the luminescence intensity changes considerably.

Effect of Light Illumination. The wave front is extremely sensitive to illumination with the exciting light when Ce^{4+} is used

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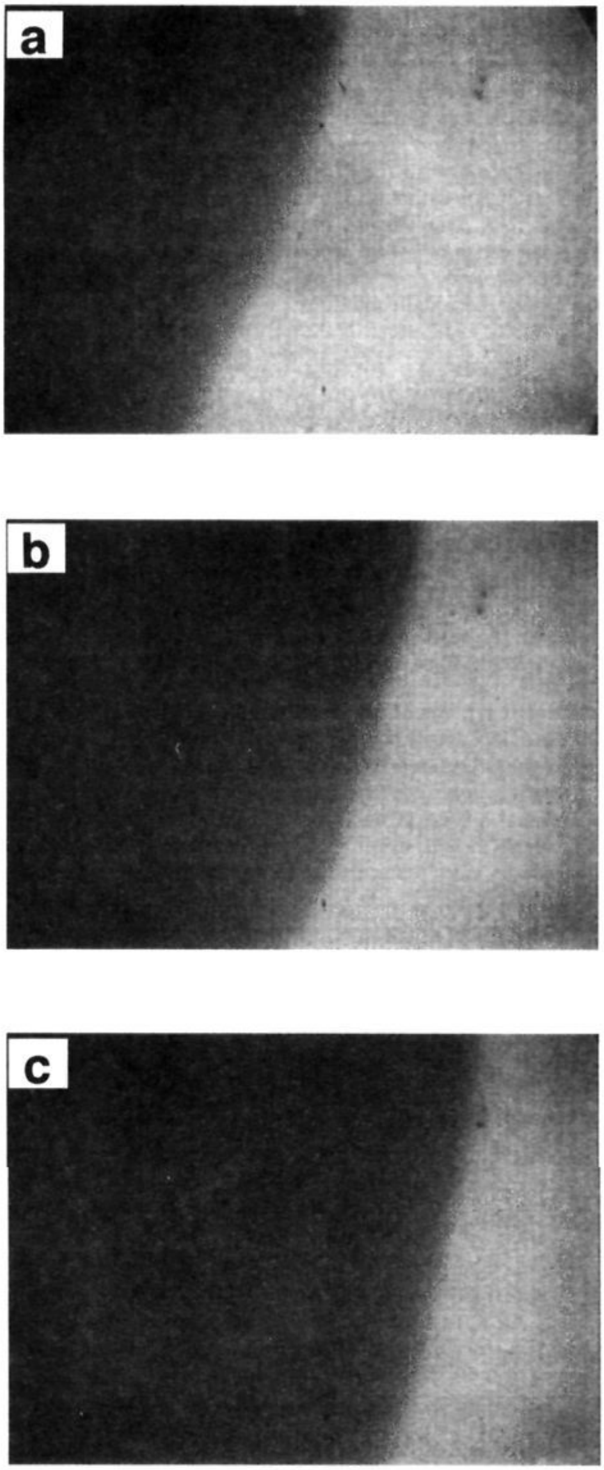

Figure 4. Time evolution of a wave front on the surface of a $Ru(bpy)_3^{2+}$ monolayer formed on a Mn^{2+}-catalyzed BZ reactor. Time elapsed between a and c: 5 s. Other experimetnal conditions are the same as in Figure 2.

as catalyst. Figure 2 shows an example of the light-sensitive wave propagation. The oxidation is completely suppressed inside the area exposed to intense illumination in the central region of the microscope field, leading to a local wave break (Figure 2b,c). The loose ends of the wave break merge as soon as the wave passes across the illuminated spot (Figure 2d), and the wave front regains its original smoothness. In contrast to this case, the wave front is totally disrupted to give two free ends when intensely illuminated by a sufficiently large light beam. Figure 3 represents the successive track of oxidized waves observed after creating broken wave fronts by strong illumination with the exciting light (intensity: 280 mW/cm^2). The light intensity for monitoring the time evolution is decreased to 68 mW/cm^2, because the entire pattern tends to fade away with higher illumination intensities due to the suppression effect. The broken ends are seen to curl into rotating spirals (Figure 3a) and then collide; consequently they coalesce to form a continuous wave front and an egg-shaped structure (Figure 3b). The latter structure moves into the area enclosed by the continuous wave front and gradually disappears if its size is too small. On the other hand, when the egg-shaped structure is sufficiently large in size, it works as a wave source and elongates into a pair of counter-rotating spirals (Figure 3c,d). These spirals collide again, and the same process recurs periodically, giving birth to a set of a closed wave front and an isolated oxidized domain. This is a characteristic feature of counter-rotating spirals with their spiral cores too close for regular spiral waves to evolve, and widely observable in pure BZ media.[4,13]

The light-controlled spatial behavior found in our experiments bears strong resemblance to that reported in the light-sensitive $Ru(bpy)_3^{2+}$-catalyzed BZ reactor[7,8] where generation and control of spiral waves were achieved by the use of a laser beam. The influence of light on this reaction system has been investigated by several researchers, and it is generally agreed that the inhibiting effect of illumination is due to the production of excess Br^- by some photochemical reactions involving the excited state of $Ru(bpy)_3^{2+}$.[14-16] The light-induced suppression of temporal oscillations in the BZ reactor/monolayer system was previously attributed to the same mechanism.[6] However, a separate set of experiments with the Ce^{4+}-catalyzed BZ reactor reveals that the presence of $Ru(bpy)_3^{2+}$ monolayer is not needed for the light-inhibition: wave breaks and spirals can be generated in thin layers of reaction solution by visible light of the same intensity as in the BZ reactor/monolayer experiment (280 mW/cm^2). To our knowledge, inhibition of the Ce^{4+}-catalyzed BZ oscillation by visible illumination has not been reported yet: Vavilin et al.[17] observed inhibiting effects under ultraviolet illumination ($\lambda <$ 300 nm), and Gáspár et al.[18] found no detectable effects with visible light emitted from a 1000-W halogen lamp. The discrepancy between these results and ours presumably arises from the difference in light intensity: The maximum illumination used in Gáspár's experiments is 225 000 lx,[18] which corresponds to a value <33 mW/cm^2 at 436 nm, about an order of magnitude smaller than the intensity employed in our experiments (280 mW/cm^2). At such high intensities it appears likely that photoexcitation of Ce^{4+} causes a notable modification in the kinetic properties of the BZ reaction. We suspect that intense visible illumination enhances the production of organic radicals by effective Ce^{4+} oxidation of malonic and/or bromomalonic acids and therefore inhibits the autocatalytic production of $HBrO_2$, increasing the amount of time the system spends in the reduced state.[19] However, exact mechanism is not clear at the present stage.

The light sensitivity of wave propagation depends on the type of catalyst in the BZ reactor. The shape of the wave front exhibits no appreciable distortion when using Mn^{2+} instead of Ce^{4+} under the same experimental conditions (Figure 4).

Photochemical Reactions in the Monolayer. Although the shape of an oxidized wave as well as its light dependence is mostly determined by the nature of the catalyst, the $Ru(bpy)_3^{2+}$ monolayer itself shows unique light sensitivity depending on

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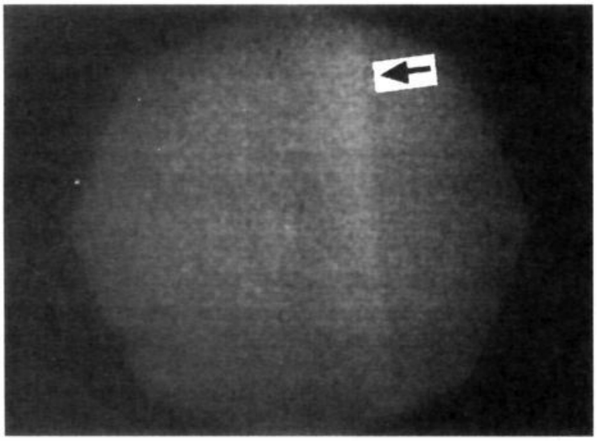

Figure 5. Light-induced reversion of imaging contrast of a $Ru(bpy)_3^{2+}$ monolayer on a Mn^{2+}-catalyzed BZ reactor with a high $[BrO_3^-]$ of 0.3 M, $[Mn^{2+}] = 0.006$ M and standard concentration of the other components (see text). The picture was taken under continuous illumination with the exciting light (intensity: 68 mW/cm^2). The white band indicated by an arrow is a wave front moving to the right side. Image area: 3.30 × 2.46 mm^2. BZ layer thickness: 0.5 mm.

subphase compositions other than the catalyst. In fact, we can obtain qualitative evidence for such behavior via a careful observation of the luminescence image under the conditions that no notable modification of the wave shape is produced.

For the monolayer on the catalyzed BZ reactor, a bright reduced background tends to get less bright under the fluorescence microscope observation by the action of visible light. The darkening of the background is much more pronounced as the initial concentration of BrO_3^- is increased. At higher BrO_3^- concentrations, there occurs quite frequently a reversion of imaging contrast between oxidized and reduced regions caused by the darkening. An example of such behavior is illustrated in Figure 5, where an oxidized wave is seen to propagate as a white band in a dark background under continuous illumination. When continuing the observation of the same field with illumination switched off before the next wave arrives, we find the original contrast, i.e., oxidized wave as dark and reduced background as bright, to reappear. Therefore, the darkening and the resulting contrast reversion are not due to irreversible process such as photodegradation of $Ru(bpy)_3^{2+}$. These findings strongly suggest the occurrence of a light-driven oxidation of $Ru(bpy)_3^{2+}$.

In contrast, the monolayer shows totally different behavior when formed on another type of reaction solution (H^+–BrO_3^-) without catalyst and malonic acid (MA). The luminescence image initially appears dark because of the oxidation of $Ru(bpy)_3^{2+}$ by BrO_3^- but rapidly turns bright on illumination with the exciting light. The brightened image gradually returns to the initial dark one after termination of illumination, again indicative of reversible photochemical process participating. The light-induced brightening can still be observed in the presence of a trace of MA. Increasing MA concentration or addition of NaBr results in a more reduced monolayer (brighter image) at the very beginning of monolayer preparation probably due to the reduction of $Ru(bpy)_3^{3+}$ by MA and/or BrMA, making it difficult to detect brightening under illumination.

As described above, the formation of spatial patterns becomes no more observable in the $Ru(bpy)_3^{2+}$ monolayer spread on the reaction solution without catalyst. In view of the light sensitivity inherent to the monolayer, it is highly possible that pattern formation which might be occuring is forced to vanish by light illumination used for microscope observation. It is also likely that the experimental conditions employed in the present study are not optimized for spatial patterns to develop in the absence of catalyst. Yamaguchi et al.[3] have demonstrated in catalyst-fixed gel systems that chemical oscillations cannot occur if the thickness of the gel is decreased below a critical value due to diffusion of chemical intermediates from the gel surface, but addition of NaBr facilitates the emergence of spatio-temporal structures. The $Ru(bpy)_3^{2+}$ monolayer coupled with uncatalyzed BZ reaction solution is an extreme case of thin catalytic system, which should require strict control of experimental constraints to achieve appropriate conditions for pattern formation.

Outlook

It has been pointed out that for BZ solutions in uncovered Petri dishes the upper layers differ from the lower ones in oscillation characteristics primarily due to diffusion of oxygen from the air, leading to complex wave behavior.[10,11,20] The present study of the BZ reactor/monolayer system shows that the peculiar nature of the interface layer can be directly visualized as two-dimensional spatial structures. Thus, the use of $Ru(bpy)_3^{2+}$ monolayer as an indicator combined with fluorescence microscopic technique provides a new experimental tool for clarifying what is actually happening at the air–water interface of BZ reaction solutions, as far as the oscillation properties of the pure BZ reactor is little affected by the presence of the monolayer.

Of course, it is of special importance to carry out a more systematic study of the BZ reactor/monolayer system for a full understanding of the dynamics of chemical reactions realized in the whole media. For obtaining further information about the complex behavior occurring in our coupled system, simultaneous observation of wave characteristics both in the monolayer and in the BZ solution would be necessary. A combination of fluorescence microscopy and two-dimensional spectrophotometry will allow such kinds of experiments, which are currently underway in our laboratory.

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