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One Dimensional Chemical Signal Diode Constructed with Two Nonexcitable Barriers

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Excitable chemical systems can process information coded in excitation pulses. Here we demonstrate the simplest realization of a chemical signal diode that transmits pulses in one direction only. It is constructed with only two different nonexcitable barriers. The proposed diode has been tested in numerical simulations and in experiments with Ru-catalyzed Belousov–Zhabotinsky reaction.

1. Introduction

Among many approaches to unconventional (non von Neumann type) computing[1] one can distinguish so-called reaction-diffusion computing[2] where the time evolution of information processing medium is described by a complex nonlinear dynamics involving the local kinetic term (reaction) and transport described by the diffusion operator. The pioneering studies in the field belong to Kuhnert, Agladze, and Krinsky who pointed out that properties of spatially distributed oscillatory chemical medium with a photosensitive reaction can be used for image processing.[3] Recent years have brought a number of results that are interesting for chemical pulse based computing. Within this approach, pulses of excitation propagating in a spatially distributed medium are interpreted as bits of information moving in space. A sequence of pulses forms a chemical signal exactly as it is in a nervous system. Information carried by these signals can be coded in the number of pulses or in times separating them. Interaction between pulses enhanced by a specially designed nonhomogeneous medium can be used to transform signals and so to process information. It has been demonstrated that various signal processing devices like logical gates,[4,5] chemical signal diodes that transmit signals in one direction only,[6,7] detectors of coincidence of pulses,[8] signal filters,[9,10] and many others can be built using the proper geometrical arrangement of the areas where the system is excitable and the nonexcitable regions where it has a single, strongly attractive stationary state so excitations decay.

Excitable chemical media play an important role in information processing functions performed by living organisms. In this respect, it seems interesting to consider alternative constructions of chemical information processing devices and study which of them are generic and may be realized in various excitable chemical systems and which are specific and restricted to reactions of a special type. It is also important to learn what are the minimum conditions necessary to build a device that performs a given function. In this paper we make a step in this direction and discuss the simplest realization of a chemical signal diode.

The classical, well-known design of a chemical signal diode is shown in Figure 1a.[6] The black areas are excitable and the white parts are not. The asymmetry required for unidirectional signal transmission is introduced by a nonsymmetrical junction formed by a rectangular active channel on one side (A) and a triangular active channel on the other (B). The distance between the top of the triangle and the side of the rectangle is selected such that a pulse of excitation propagating in the rectangular channel gives sufficiently strong perturbation to excite the triangle tip and thus the excitation can be transmitted from A to B. On the other hand, the physical size of a pulse moving in B channel toward the top of the triangular part decreases. The amplitude of excitation (the peak value of activator concentration) also decreases, because the diffusion of activator to the nonexcitable region becomes more important when the channel becomes narrow. Therefore, the perturbation generated by a pulse in the triangular channel is too small to excite the channel A. As the result the junction shown in Figure 1A transmits excitations in one direction only. The design of such chemical signal diode is generic (it can be adopted for any excitable chemical system), but the excitability of the medium depends on two space variables.

A few years ago, it was discovered that the diode can be also constructed in one-dimensional systems.[11] The authors considered a system in which excitability depends on a single spatial variable x, whereas it does not change in the other directions. Using numerical simulations based on the Oregonator model of the Ru-catalyzed Belousov–Zhabotynsky (BZ) reaction (eqs 1–3[12]), they have shown that the amplitude and slope of the illumination profile described by a triangular function (cf. Figure 1B) can be adjusted such that a pulse of excitation is transmitted in one direction only. The Ru-catalyzed BZ medium becomes less excitable if illumination increases. If the catalyst is immobilized, then pulses that entered the illuminated area from the strongly illuminated site are not transmitted, whereas the pulses propagating in the other direction can pass through.

In this paper we continue the study on one-dimensional chemical signal diode and present yet a simpler realization of it. In our design, the diode is composed of just two nonexcitable areas with different excitabilities (called strongly and weakly illuminated areas), but unlike in the system studied by Toth et al.,[11] the illumination within each of these areas is uniform (cf.

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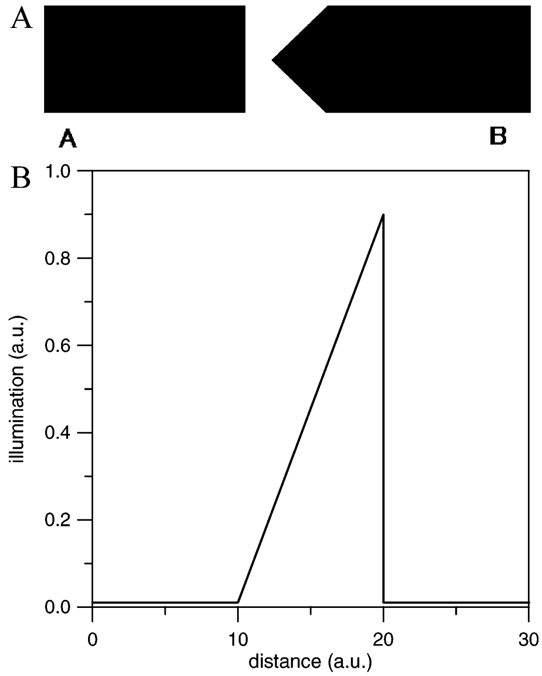

Figure 1. Previously published constructions of the chemical signal diode. (A) Spatial distribution of excitable (black) and nonexcitable (white) regions in a two-dimensional chemical diode. (B) Illumination profile as a function of space variable in one-dimensional diode considered in ref 11.

Figure 2, parts A and B). It is hard to imagine a simpler construction of a signal diode, because the device has to be unsymmetrical to perform its function. We demonstrate that the considered diode works using numerical simulations based on the Oregonator model. The diode built with two illumination steps is much simpler for an experimental realization than the one based on the triangular illumination function. We present and discuss experimental results that nicely agree with the predictions of numerical simulations.

2. Numerical Simulations

In simulations we use 3-variable Oregonator model, adopted for the photosensitive ruthenium catalyzed BZ reaction:[13]

$$\epsilon_1 \frac{\partial u}{\partial t} = u(1-u) - w(u-q) + D_u \Delta u \tag{1}$$

$$\frac{\partial v}{\partial t} = u - v \tag{2}$$

$$\epsilon_2 \frac{\partial w}{\partial t} = \Phi + fv - w(u+q) + D_w \Delta w \tag{3}$$

where u, v, and w are dimensionless concentrations of $HBrO_2$, $Ru(4,4'\text{-dm-bpy})_3^{3+}$ and Br^-, respectively. The units of space and time are dimensionless and they have been chosen to scale the reaction rates and the diffusion coefficient D_u(=1). We have neglected the diffusion of the ruthenium catalytic complex because it is much smaller than that of the other reagents. For simplicity we set $D_w = 1$. The parameter Φ represents the rate of bromide production caused by illumination and it is proportional to the applied light intensity. Br^- is an inhibitor of Ru-catalyzed BZ reaction so the regions with a low illumination levels are excitable and those where illumination is high are not. Therefore, by adjusting the value of Φ we can create areas with the required level of excitability. The values of the other parameters of the model q, ϵ_1, and ϵ_2 have been selected as: 0.002, 0.08, and 0.00097 respectively. In order to check if the parameters can influence the function of the diode we considered two types of Oregonator models with $f = 1.12$ and $f = 2.12$. These values seem to match better our experimental conditions than $f > 2.3$ commonly used in the literature,[11,14] because they predict oscillations if the system is not illuminated, which agrees with the experiments.

Equations 1−3 have been solved numerically by the 4th order Runge−Kutta method for the chemical kinetics combined with the explicit Euler algorithm for diffusion. The diode is composed of two regions characterized by different illumination level. The boundary between these regions has been always placed in the center of the grid. In simulations we have used one-dimensional grid consisting of 2000 points. It has been verified that for the selected spatial and temporal steps of integration (0.075 and 0.00005 respectively) the results of simulations are stable numerically. No-flow boundary conditions at the ends of the system have been applied.

In order to observe if the diode performs its function, we have studied the evolution of pulses propagating in both directions. The pulses are initiated by setting the value of u equal to 0.4 at two grid points at one of the ends. Parts A and B of Figure 2 show one of the considered realizations of the simplified chemical signal diode. It is composed of 41 grid points long interval where $\Phi = 0.045$ and 41 grid points long interval where $\Phi = 0.03$. The excitable medium around is characterized by $\Phi = 0.008$. The calculations has been performed for $f = 1.12$. Parts C and D of Figure 2 illustrate the time evolution in the central area in the form of space-time plots. Light areas correspond to a high concentration of u and so they represent a propagating excitation. It can be seen that an excitation coming from the weakly illuminated area to the strongly illuminated area is transmitted (Figure 2D), whereas the one propagating in the reverse direction is stopped (Figure 2C). It is worth noticing that this particular system is highly symmetrical in the sense that the widths of both nonexcitable regions are equal and the asymmetry comes from difference in illumination levels only. One can also see that for some time after crossing the barriers (for times around 23 time units in Figure 2D), the excitation splits out. In the case presented, the pulse propagating backward dies in the nonexcitable barrier and it does not influence the work of the diode. However, the interesting phenomenon of pulse splitting on a barrier may be used in other chemical signal processing devices. We have performed a number of simulations to check what is the working range of widths of nonexcitable areas for which the signal diode works. The results obtained for $f = 2.12$, $\Phi = 0.0007$ in the of excitable medium, and nonexcitable medium characterized by $\Phi = 0.01$ and $\Phi = 0.02$ are summarized in Figure 3. These results indicate that the size of strongly illuminated area is important and it has to be selected with a high precision. For the selected illuminations the diode action is observed only when the width of strongly illuminated areas is within 3.075 and 3.3 distance units. On the other hand if the width of strongly illuminated region is properly selected then the construction of one-dimensional chemical signal diode is quite tolerant of the width of the weakly illuminated region (in our case the diode function is observed within 2.0 and 15 distance units).

3. Experimental Results

We have tested whether the simplified diode works in experiments with Ru-catalyzed BZ reaction. The propagation of excitation pulses have been studied on a cellulose-nitrate

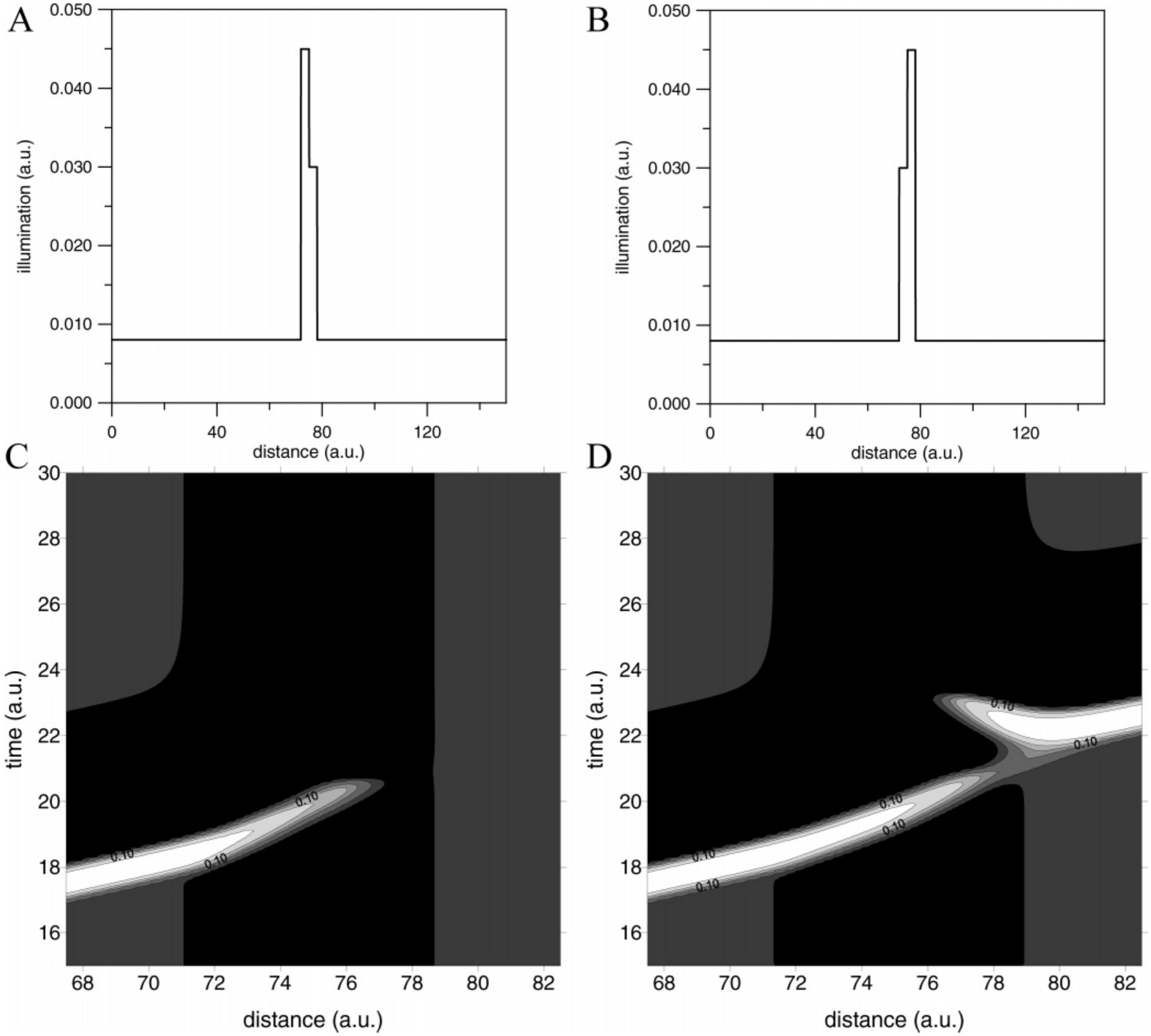

Figure 2. Numerical simulations of the simplified one-dimensional diode. (A, B) Rate of bromide production $\Phi(x)$ as a function of space variable. $\Phi(x)$ shown in part B is the mirror reflection of that from part A. (C, D) Time evolution of a pulse in the neighborhood of the diode for $\Phi(x)$ from parts A and B. In these space-time plots light shading indicates a high concentration of the activator u, gray corresponds to the concentration of activator in relaxed excitable medium, and black characterizes the concentration of activator in nonexcitable areas.

membrane filters (A100A025A, 2.5 cm diameter, Advantec) with a pore size of 1 μm. The membrane was filled with the following solution: 50 μL of H_2O, 400 μL of $NaBrO_3$ (1.5 M), 100 μL of H_2SO_4 (3.0 M), 200 μL of malonic acid (1.0 M), 50 μL of KBr(1.0 M), and 200 μL of $Ru(bpy)_3Br_2$ (8.5 mM). The soaked membrane was placed on a glass plate and immediately covered with silicon oil to prevent it from drying and to protect from the influence of oxygen.

During the experiment, the membrane was illuminated from the bottom using a slide projector as a light source. The illumination level has been controlled by the distance between projector and the membrane and by a transparent film with a printed shape of the diode (cf. Figure 4A). Black printed areas of the film have formed the excitable channels on the membrane. The strongly illuminated area of the diode has been created by a clear part of the film and the weakly illuminated area has been obtained where the film has been printed gray. In order to observe propagation in each direction under the same conditions we have studied the set of two diodes with different orientations in a single experiment as shown in Figure 4B. The diodes were placed close one to another in order to reduce a possible nonhomogenity of light. Estimated illumination levels in the excitable channels, the weakly illuminated and the strongly illuminated areas have been 10 klx, 37 klx and 97 klx respectively. Pulse propagation has been observed under a microscope and the image has been registered by a digital video camera and analyzed using standard imaging processing techniques. For the image enhancement, a blue optical filter has been used. Results of the experiment are shown in Figure 5 and they confirm predictions of simulations. We have observed that the barrier composed of two nonexcitable regions can work as a chemical signal diode, and it transmits pulses arriving from the site at which excitability is higher.

The experiments have also demonstrated another interesting property of the diode. It can be noticed (cf. Figure 5) that the first three arriving pulses have passed through the diode but

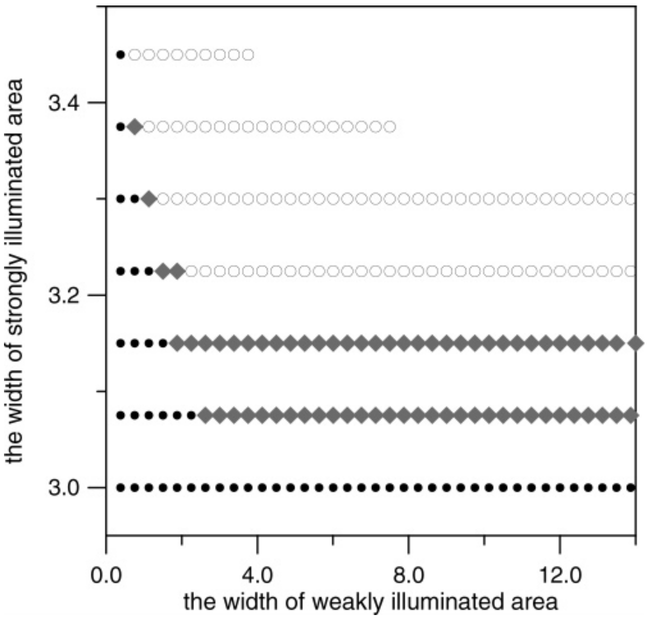

Figure 3. Function performed by two barrier system as the function of widths of weakly ($\Phi = 0.01$) and strongly ($\Phi = 0.02$) illuminated areas. The excitable channels are characterized by $\Phi = 0.0007$ and $f = 2.12$. Empty circles mark combinations of widths for which the system stops all pulses, dots dentote transmission in both directions, and diamonds represent signal diodes.

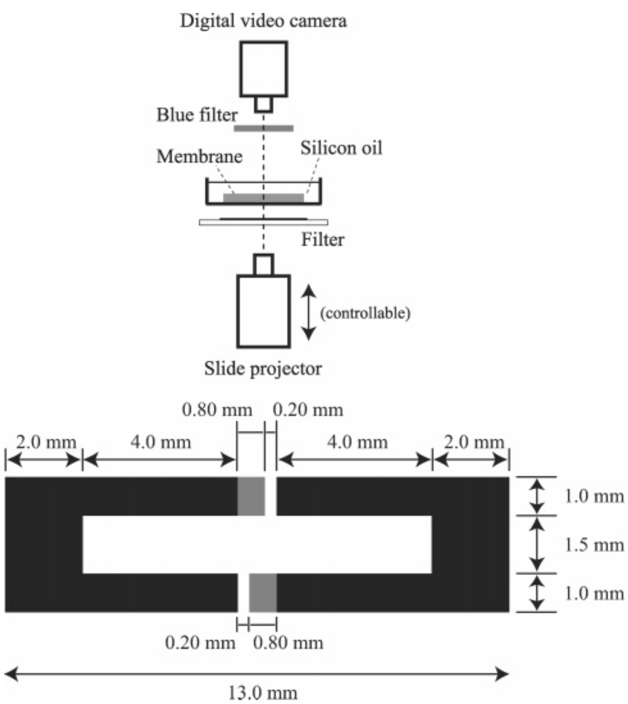

Figure 4. (A) Schematic representation of the experimental setup. (B) Geometry of excitable channels and barriers used in the experiment.

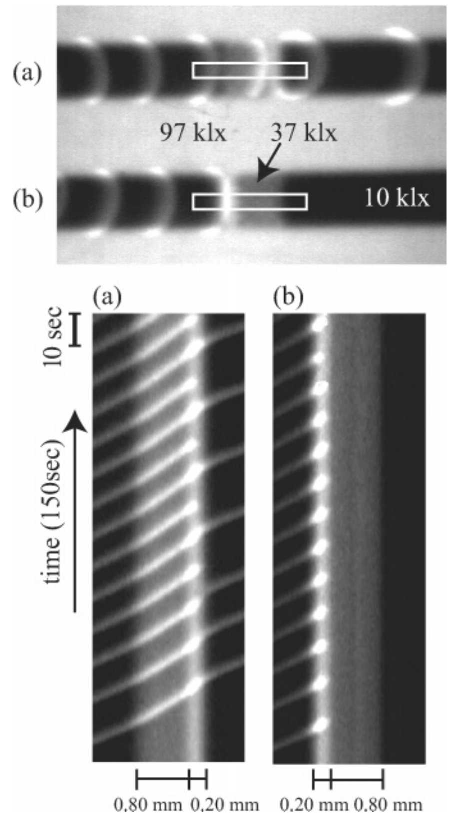

Figure 5. Experimental results. Light areas denote a high concentration of Ru(4,4′-dm-bpy)$_3^{3+}$. The upper figure shows a snapshot from experiment with areas as in Figure 4B; the lower figure is a space-time plot showing the evolution of excitations in the areas marked above.

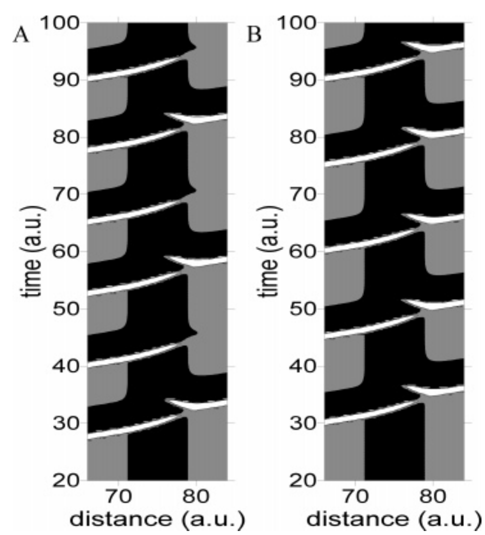

Figure 6. Space-time plot showing the evolution of u for two different frequencies of incoming excitations. The diode is formed with a strongly illuminated area (41 grid points with $\Phi = 0.045$) and a weakly illuminated one (43 grid points with $\Phi = 0.03$), $f = 1.12$.

later only every second of the incoming pulses has been transmitted. A frequency transformation on a nonexcitable barrier is a well-known effect.[15] It depends on the frequency of incoming pulses.[16] In the experiment, it can bee seen that the frequency of arriving pulses suddenly increased (they were generated by a silver wire in a medium outside the observed area) and as the result the frequency of outgoing signal has dropped. The same effect can be easily obtained in numerical simulations. Parts A and B of Figure 6 compare the results obtained for the system composed of two barriers (41 grid points with $\Phi = 0.045$ and 43 grid points with $\Phi = 0.03$) and $f = 1.12$. In both cases a periodic train of excitation pulses arrives at the diode; in Figure 6, the time difference between excitations is 12.5 time units, and in Figure 6B, it is 15 time units. Like in the experiments, for the lower frequency the input signal has passed unchanged, whereas for the higher input frequency only half of the pulses have been transmitted.

4. Discussion

In this work, we have described the simplest chemical signal diode composed of just two areas characterized by different excitability. We have performed numerical simulations for two sets of parameters and in both cases the observed direction of transmission: from low to high illumination is the same. The direction in which the diode transmits chemical signals agrees with the results obtained for a diode characterized by a triangular illumination studied by Toth et al.[11] We have also found that the width of strongly illuminated area has to be chosen with a high precision, whereas the size of weakly illuminated area is not that important. The results of our computer simulations have been nicely confirmed with the experiments.

We believe that the construction of the chemical signal diode based on two stripes of nonexcitable medium is generic and can be adopted to other excitable systems. A pulse is transmitted through a nonexcitable barrier if the perturbation of the excitable medium on the other side of a barrier is strong enough to excite the medium. Dumping a signal in a nonexcitable barrier has a nonlinear character and it strongly depends on the amplitude of the arriving signal. Therefore, it is not unusual for two barriers that the amplitude behind the diode depends on the order of barriers.

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