

# Wave initiation in the ferroin-catalysed Belousov–Zhabotinsky reaction with visible light

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The initiation of chemical reaction–diffusion waves by visible light of wavelength  $\lambda = 632.8$  nm from a 20 mW He–Ne laser in the ferroin-catalysed BZ reaction on a polysulfone membrane is reported. With low loading of the catalyst on the membrane, oxidation waves can be initiated from the resting steady state and in the recovering tail of a wave. With high loading, waves can only be initiated in the ‘vulnerable’ region behind an existing wavefront. The mechanism of this initiation is discussed in terms of the photoreduction of the metal–ligand catalyst and expressed in terms of a modified Oregonator model. These new observations are in contrast to the inhibitory effect of visible light in the light-sensitive Ru-catalysed BZ system.

## Introduction

The Belousov–Zhabotinsky (BZ) reaction provides a chemical example of an *excitable medium* and is widely exploited to study the generic behaviour of such systems. Excitable media in a wider context include cardiac muscle,<sup>1</sup> neuronal tissue,<sup>2</sup> heterogeneous catalysts<sup>3</sup> and flames.<sup>4</sup> The propagation of chemical waves, and the spatial reaction–diffusion structures they may create, are of particular interest, and are believed to be related to cardiac arrhythmia and other pathological responses.<sup>5</sup>

The effect of light on the BZ system has been studied for over 30 years. Vavilin *et al.*<sup>6</sup> showed the suppression of oscillations in the cerium-catalysed reaction. Busse and Hess<sup>7</sup> initiated waves in the ferroin-catalysed system using u.v. illumination. A ‘light-sensitive’ BZ system can be constructed using the tris(2,2’-bipyridine) ruthenium(II), Ru(bpy)<sub>3</sub><sup>2+</sup>, and is sensitive to both u.v. and visible radiation.<sup>8–15</sup> Gáspár *et al.*<sup>16</sup> investigated the effects of visible light on BZ systems with various catalysts, showing that both the ferroin and ruthenium systems are sensitive in this region, but that the cerium system is unaffected. The Ru(bpy)<sub>3</sub><sup>2+</sup> system has been widely exploited and the mechanism through which light of wavelength  $\lambda = 452$  nm influences the reaction by providing an additional channel for the production of the inhibitor bromide ion species seems well established.<sup>17–19</sup> The light-sensitivity of the ferroin system has been relatively under-exploited, although it has been recently used to manipulate spiral waves in an open reactor.<sup>20</sup> In this communication, we report on a new method for the photo-initiation of oxidation waves in the ferroin-catalysed BZ system, using visible radiation from a He–Ne laser ( $\lambda = 632.8$  nm).

## Experimental

We exploit a ‘membrane reactor’ system following Lázár *et al.*<sup>21</sup> A circular polysulfone membrane (Gelman: pore size

0.45  $\mu\text{m}$ , 47 mm diameter) is loaded with the redox catalyst, bathoferroin. A ‘low loaded’ membrane is prepared by dissolving 10 mg of bathophenanthroline (4,7-diphenyl-1,10-phenanthroline, Aldrich) in 5 cm<sup>3</sup> of glacial acetic acid. The membrane is then dipped in this solution for *ca.* 2 s. The membrane is then immersed and agitated in a 20.0 cm<sup>3</sup> solution of 0.002 M Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> in 0.2 M H<sub>2</sub>SO<sub>4</sub>. A ‘high loaded’ membrane is prepared in a similar manner, but with 50 mg of the ligand.

The prepared membrane is washed in distilled water for 20 min. For the reaction, it is immersed in a catalyst-free BZ solution in a Petri dish. The initial composition of this solution used in this work is: [MA] = 0.213 M, [NaBrO<sub>3</sub>] = 0.213 M, [H<sub>2</sub>SO<sub>4</sub>] = 1.596 M, [NaBr] = 0.162 M and [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] = 0.64 M, where MA = malonic acid. This composition is similar to that used by Lázár *et al.* except that the acid concentration is increased by a factor of 3.

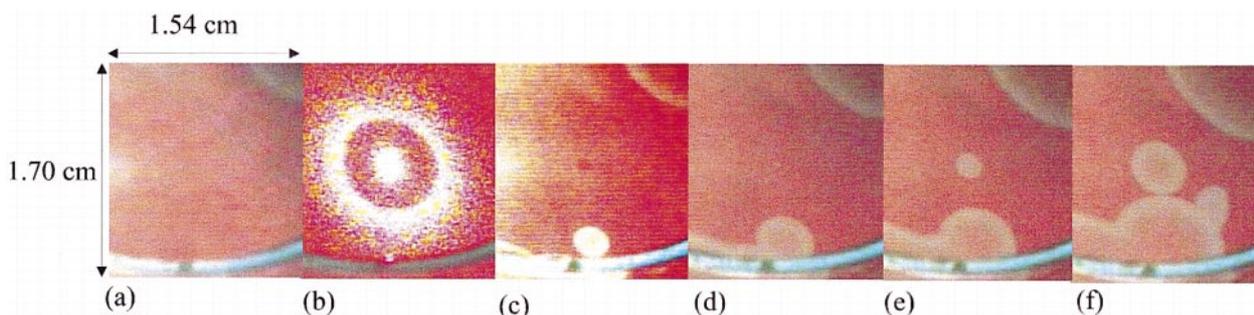
Spontaneous initiation of oxidation waves (typically at the edge of the membrane) is observed in this system, but the main feature of the present work is the illumination of small regions of the membrane by light from a He–Ne laser (nominal power = 20 mW,  $\lambda = 632.8$  nm). Images are then captured using a video camera onto a computer and analysed as described previously.<sup>22</sup>

## Results

### (a) Low-loading of membrane

Fig. 1–3 show the effect of illumination on the evolution of a ‘low-loaded’ membrane in three different scenarios. In Fig. 1(a) the region of the membrane in the frame is in the ‘resting’ steady state, undisturbed by any oxidation wave. Although this corresponds to the reduced (red) state, previous measurements with these reactant concentrations in thin solutions indicate that there is a relatively high background concentration of the oxidised form of the catalyst as well. Following illumination for 5 s, Fig. 1(b), a circular region of diameter  $\sim 1$  mm, which is visibly a ‘deeper’ red, Fig. 1(c), is developed (this is observed immediately after the laser is turned off and presumably develops during the irradiation). From this site, an oxidation front develops, Fig. 1 (d, e, f), and grows as a circular pulse. In the absence of further illumination, no subsequent initiation occurs. The important observation here, therefore, is that illumination in this case enhances the reduction of the redox catalyst.

A similar response is observed if the illumination is provided in a region of the membrane sufficiently long after the passage of an oxidation front. In Fig. 2, the initiation of a

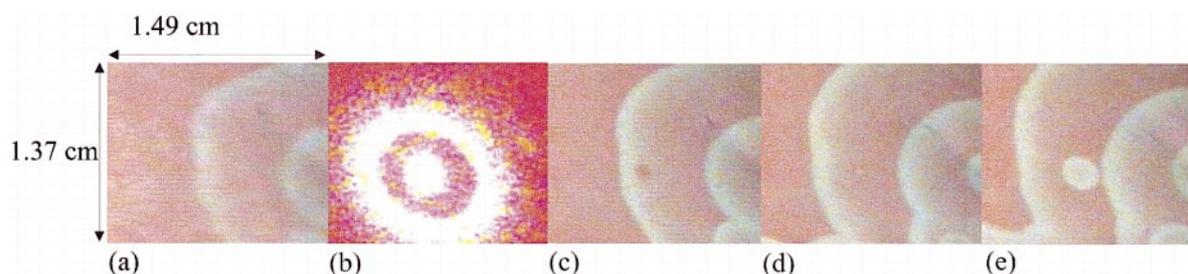


**Fig. 1** Effect of illumination on the resting steady state membrane with low loading: (a) before perturbation showing reduced steady state; (b) illumination by laser for 5 s (illuminated area = *ca.* 2 mm<sup>2</sup>); (c) at  $t = 6$  s after illumination turned off, enhanced reduction in perturbed region of area *ca.* 0.8 mm<sup>2</sup>; (d) onset of oxidation in perturbed region (blue) at  $t = 16$  s; (e)  $t = 26$  s and (f)  $t = 40$  s, growth of circular wave.

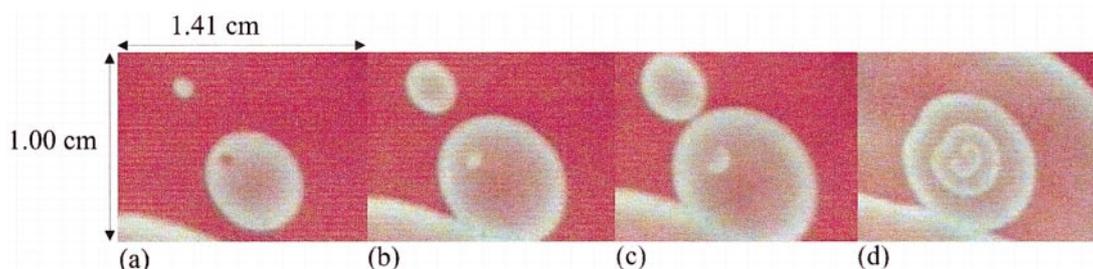
circular pulse is shown. The illumination is applied to a location approximately 3 mm behind an expanding front in a target pattern. The enhanced reduction of the illuminated region is clearly visible in Fig. 2(c) with the initiated expanding circular wave having developed by image (e).

In Fig. 3, the illumination is provided somewhat closer to an existing oxidation front. The illuminated region is revealed by the enhanced extent of reduction behind the blue oxidation

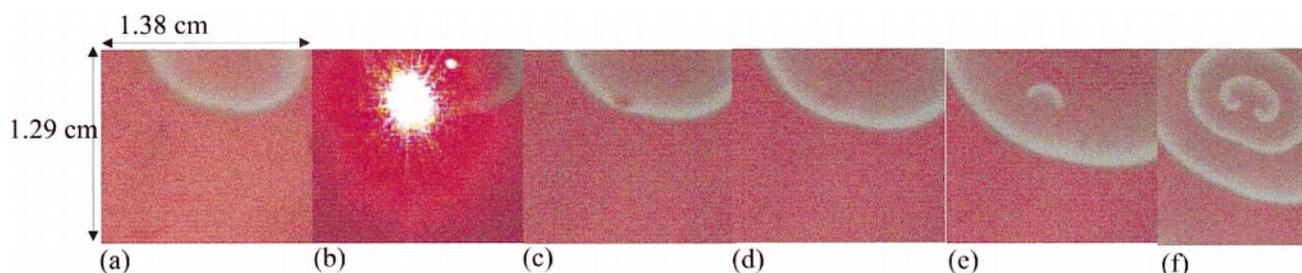
pulse approximately in the centre of Fig. 3(a). As an oxidation front then develops from this initiation site, so the region of this front developing in the 'north-westerly' direction runs into a region of high inhibitor concentration created by the original pulse, Fig. 3(b). This causes the nascent circular wave to break. The segment propagating in the opposite direction to the original front, however, encounters a sufficiently recovered composition so as to develop successfully. This leads to



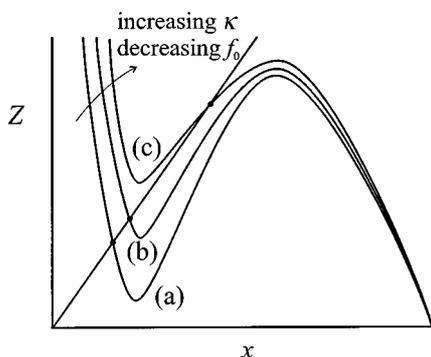
**Fig. 2** As in Fig. 1: (a) a 'spontaneous' oxidation wave is propagating from right to left across the field of view; (b) illumination by laser for 5 s; (c) at  $t = 6$  s after illumination turned off, showing region of enhanced reduction (red) in wave tail; (d)  $t = 18$  s, onset of oxidation in perturbed region; (e)  $t = 32$  s, growth of initiated wave.



**Fig. 3** As in Fig. 2, following illumination closer to existing oxidation wave: (a) immediately after illumination turned off, showing region of enhanced reduction (red) in wave tail; (b)  $t = 10$  s, onset of oxidation in perturbed region; (c)  $t = 14$  s, development of initiated wave, showing asymmetric evolution, with failure of propagation in the direction following original wave, leading to development of spiral wave pair; (d)  $t = 62$  s, sustained wave initiation from spiral pair.



**Fig. 4** As in Fig. 3, but for higher loaded membrane: (a) spontaneous wave propagating from top of image; (b) illumination by laser for 3 s; (c) at  $t = 6$  s after illumination turned off, showing region of enhanced reduction (red) in wave tail; (d)  $t = 16$  s, onset of oxidation in perturbed region; (e)  $t = 46$  s, development of initiated wave, showing asymmetric evolution, with failure of propagation in the direction following original wave, leading to development of spiral wave pair; (f)  $t = 190$  s, sustained wave initiation from spiral pair.



**Fig. 5** Schematic representation of light intensity on the nullclines in the  $x$ - $Z$  phase plane for the modified Oregonator model: increasing the light intensity shifts the  $x$ -nullcline to lower values in the phase plane as the parameter  $f_0$  decreases. Curve (a), unperturbed system with high value for  $f_0$  ( $=f$ ) with steady state intersection point lying far from minimum in  $x$ -nullcline. The threshold for excitation (the middle branch of the  $x$ -nullcline) lies far to the right of the steady state. Curve (b), with illumination,  $f_0 < f$ : the steady state lies close to the minimum in the  $x$ -nullcline, indicating a more excitable system with a lower threshold of excitation. Curve (c), with higher illumination, the intersection may move onto the middle branch, corresponding to a spontaneously oscillatory system under illumination.

the creation of a pair of counter-rotating spirals, Fig. 3 (d, e) which continue to initiate subsequent waves even without further illumination.

### (b) High-loading of membrane

Similar experiments have been performed with the high-loaded membrane. Illumination in the resting or recovered states equivalent to Fig. 1 and 2 does not, now, lead to initiation of oxidation structures. The ‘vulnerability’ of a region sufficiently close to an existing oxidation pulse, however, is still evident, and is illustrated in Fig. 4. The creation of spiral pairs in this manner is identical in methodology to that reported by Gómez-Gesteira *et al.*,<sup>23</sup> who perturbed a BZ system in the rear of an oxidation front using electrochemical removal of bromide ion with an Ag wire.

### Mechanism of initiation

The experimental observations reported here show that visible light of the appropriate frequency can be used to initiate oxidation in the ferroin-catalysed BZ reaction. Such an effect complements existing methods using Ag wires or other electrochemical perturbations: the ease of producing precisely controlled illumination fields suggests that this new method may have great flexibility for future studies of BZ waves. The effect of light here is also complementary to the quite different, inhibitory effect observed for the  $\text{Ru}(\text{bpy})_3^{2+}$  system and from the essentially inhibitory effect noted in ref. 20.

No definitive conclusions can be drawn from the above observations concerning the precise nature of the mechanism through which visible light of wavelength  $\lambda = 632.8$  nm leads to initiation in the ferroin-catalysed BZ system. However, some suggestions can be made on the following basis. The reduced form of the catalyst shows a broad, strong absorption peak<sup>24</sup> with maximum absorbance at  $\lambda = 510$  nm with  $\epsilon_{\text{max}} = 11\,100 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , but does not absorb significantly in the red end of the visible spectrum. The blue, oxidised form of the catalyst, however, has an absorption maximum<sup>25</sup> at  $\lambda = 590$  nm with  $\epsilon_{\text{max}} = 600 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ . This band extends to the wavelength of the light used here. The ferroin is, then, clearly the more likely absorber. Photo-reduction of  $\text{Fe}(\text{phen})_3^{3+}$  proceeds at this wavelength with a quantum efficiency of *ca.*  $2 \times 10^{-2}$  in 0.05 M  $\text{H}_2\text{SO}_4$  in the presence of organic reducing species such as formate ion.<sup>26,27</sup> The reduction is believed to proceed through the formation of a ligand–metal charge transfer (LMCT) excited state with elec-

tron transfer from the solvent. Intramolecular photo-oxidation processes also arise, but this is a rarer process as ligands are generally more reducing than the central metal ion.

A simple extension of the classic 2-variable Oregonator model can be proposed on this basis, incorporating an additional, light-sensitive step removing the oxidised form of the catalyst with no corresponding production of bromide ion:



The resulting dimensionless equations for the autocatalyst concentration  $x$  and oxidised catalyst concentration  $z$  for a well-stirred system can then be written as

$$\epsilon \frac{dx}{dt} = x(1-x) - fz \frac{(x-q)}{(x+q)}, \quad \frac{dz}{dt} = x - (1 + \kappa(\phi))z$$

where the various symbols correspond to the Tyson–Fife scalings<sup>28</sup> for this model and the parameter  $\kappa$  is the dimensionless rate coefficient for step (1) above and depends on the illuminating light intensity  $\phi$ .

These equations can be re-scaled by introducing  $Z = (1 + \kappa)z$ ,  $\epsilon_0 = (1 + \kappa)\epsilon$  and a time  $\tau = (1 + \kappa)t$ , yielding

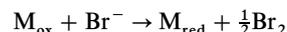
$$\epsilon_0 \frac{dx}{d\tau} = x(1-x) - f_0 Z \frac{(x-q)}{(x+q)}, \quad \frac{dZ}{d\tau} = x - Z$$

This is the classical Oregonator form, with a modified stoichiometric factor

$$f_0 = f/(1 + \kappa)$$

Increasing the light intensity and, hence, the value of  $\kappa$  leads to a reduction in the (local) value of the effective stoichiometric factor. As the resting state of the un-illuminated system in the present work corresponds to a relatively high value for  $f$ , the effect of illumination is to reduce the local steady-state concentration of the oxidised form of the catalyst and, consequently, of the inhibitor  $\text{Br}^-$ . The threshold for excitation, in terms of the autocatalyst concentration required to initiate and oxidation event, is also substantially reduced for the illuminated system compared to the unperturbed steady state, as indicated in Fig. 5. A sufficiently large shift in the effective stoichiometric factor may even produce a region that is locally spontaneously oscillatory.

This explanation, therefore, involves a local reduction of the redox catalyst and a reduction of the steady state concentration of  $\text{Br}^-$ . This effect arises through decreasing the rate of  $\text{Br}^-$  production through process C by providing a competing channel for removal of  $\text{M}_{\text{ox}}$ . An alternative (or additional) possibility would be that the photo-excited state of the catalyst might have an enhanced reactivity to  $\text{Br}^-$ . The step



has been incorporated for the ferroin-catalysed system in an extension for the bromate–ferroin system under CSTR operation.<sup>29</sup> This step enhances the rate of catalyst reduction and reduces the steady state concentration of bromide ion.

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