Photophobic and phototropic movement of a self-oscillating gel†

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A photosensitive self-oscillating gel that incorporates the Belousov–Zhabotinsky reaction can undergo rhythmic mechanical oscillations. We exploit the dependence of the oscillation frequency on light intensity to generate both photophobic and phototropic movement of the gel under differential illumination. Our findings may be used in designing intelligent sensors that can execute biomimetic behaviours.

The design and fabrication of intelligent artificial soft materials has attracted considerable attention in recent years.1 Of particular interest are systems that can execute biomimetic behaviours, such as fleeing adverse stimuli and approaching favourable environments, as observed in photophbic and phototropic organisms.2,3

In an effort to develop intelligent responsive materials, Yoshida et al.4 coupled a soft polymer with a chemical reaction to yield a biomimetic system capable of executing swelling–shrinking oscillations without external stimulation. In this scheme, ruthenium(II) tris(2,2′-bipyridine) (Ru(bpy)3), the photosensitive catalyst of the oscillatory Belousov–Zhabotinsky (BZ) reaction, is copolymerized with N-isopropylacrylamide (PNIPAAm) to form a gel that can shrink and swell in response to changes in the redox state of the catalyst. This material thus undergoes an autonomous swelling and deswelling driven by the chemically oscillating BZ reaction5 occurring within the network of polymer. Moreover, the light-sensitive character of the catalyst within the copolymer can be utilized to modulate the dynamical behaviour of the gel.6 Balazs and coworkers developed a detailed model7 of such BZ gels that incorporates both the chemistry of the BZ reaction and the mechanical aspects of the gel. They subsequently augmented the model to investigate the effect of light on BZ gels and carried out simulations to demonstrate that these materials can exhibit spontaneous movement away from an illuminated region.8

The above studies of the effects of illumination on BZ gels focus on photoinhibition,9 i.e., oscillations in the BZ reaction are suppressed at high light intensity, as the inhibitor (Br−) is produced in the following reaction:

\[
\text{Ru(bpy)}_3^{2+} + \text{BrMA} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Br}^- + \text{products}
\]

where Ru(bpy)32+ is a photoexcited state of the catalyst. However, the ruthenium-catalyzed BZ reaction may also exhibit photoinduction10 by generating the activator species, HBrO2:

\[
\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} + \text{BrO}_3^- + \text{H}_2\text{O} \rightarrow \text{HBrO}_2 + \text{H}_2\text{O} + 2\text{Ru(bpy)}_3^{3+}
\]

whether photoinhibition or photoinduction dominates depends primarily on the light intensity. In a stirred batch reactor, we found that the dependence of the oscillation frequency on light intensity is nonmonotonic. The reaction was run in a thermostated (T = 22.0 ± 0.1 °C) quartz glass reactor with total volume 10.0 mL and was illuminated by an LED source (λmax = 460 nm). The light intensity was controlled by a digital control unit and calibrated with a photometer (Model 1L1400A, International Light). The optical path length was 2 cm. The reactor was stirred at 500 rpm with a Teflon-coated magnetic stirrer. The oscillations can last for more than 10 h. We utilized the stable oscillations with almost constant frequency, which persist for about 2.5 h in the absence of illumination, to test the effect of light intensity on the oscillatory frequency. The oscillations were monitored with an ORP electrode (Thermo Fisher). Raw data for typical oscillations at several light intensities are shown in Fig. S1 (ESI†). At low levels of illumination, the frequency increased with intensity, as seen in the positive slope region of curve a in Fig. 1. Above about 390 μW cm−2, the frequency decreased along the negative slope region of the curve, and ultimately oscillations ceased.

We carried out simulations with a two-variable batch Oregonator model, which describes both photoinduction and photoinhibition in the ruthenium-catalysed BZ reaction and

† Electronic supplementary information (ESI) available: Movie S1 and Movie S2 show the photophobic and phototropic movements, respectively. See DOI: 10.1039/c3cc44480e
is derived from a three-variable photosensitive Oregonator model. Details of the model and simulations are given in the ESI. The results of simulations with this model (curve b of Fig. 1) were qualitatively similar to the experiments. However, simulations without the photoinduction factor yielded oscillatory frequencies that decreased monotonically, as shown in curve c of Fig. 1.

BZ gels undergo a net displacement that is opposite to the propagation of traveling waves, since these waves “push” the solvent away from the wave source. Among regions of different oscillatory frequencies, the highest frequency determines the ultimate direction of motion of the wave. Therefore one might expect that the movement of an illuminated BZ gel can be switched between photophobic and phototropic mode by adjusting the illumination distribution. If so, it should be feasible to optically control the movement of a BZ gel, since this behaviour derives from the intrinsic dynamics of the BZ oscillations.

In this work, we synthesised a photosensitive gel (poly(NIPAAm-co-Ru(bpy)₃-AMPS)) inside a capillary. The details of the synthesis are given in the ESI. SEM micrographs of this pseudo-one-dimensional gel are shown in Fig. 2. The honeycomb-like microstructure of poly(NIPAAm-co-Ru(bpy)₃-AMPS) provides a locally open reaction–diffusion medium that is free from convection effects.

The responsive gel in a capillary with both ends open was soaked in a 20.0 mL mixture of catalyst-free BZ solution containing malonic acid (MA), HNO₃, NaBr and NaBrO₃. The temperature was maintained at 22.0 ± 0.1 °C. The gel was illuminated by an LED source (λ_max = 460 nm). Traveling waves initiated spontaneously at both ends. The spatiotemporal evolution of the pulse waves was recorded with a charge-coupled-device (CCD) camera (TUSEN, TCC-1.4CHICE) connected to a computer. The images were recorded along the capillary at different times, and a time series of the local dynamics was obtained as grey values proportional to the concentration of the oxidised form of the catalyst at a specific location. The 460 nm LED light is absorbed by Ru(bpy)₃²⁺ solution but transmitted by Ru(bpy)₃³⁺ solution. The CCD grey values are proportional to the transmitted intensity, hence to the concentration of the oxidised form of the catalyst. For producing photophobic and phototropic movement, patterned illumination was introduced to modulate the oscillation frequency of the BZ gel. We constructed different configurations of brighter and darker regions to generate photopromotion and photoinhibition effects. Fig. 3 and 4 show two different types of nastic-like movements in response to differential illumination. In the first case (Fig. 3), the right half of the capillary was kept in the brighter region (I = 904.0 µW cm⁻²) and the left half in the darker region (I = 205.0 µW cm⁻²). Pulse waves appeared in both halves of the gel, which periodically swelled and deswelled at the oscillatory frequency of the pulses.
Under this condition, the frequency in the weakly illuminated region was higher than that in the brighter region (Fig. 3a). This difference in mechanoresponsiveness between weakly and strongly illuminated regions breaks the force equilibrium in the gel. Ultimately, the BZ gel was spontaneously drawn away from the bright region and moved toward the dark region as shown in Fig. 3b. This experimental observation is consistent with the behaviour predicted by Dayal et al.\(^\text{8}\) in their model simulations. Fig. 3c shows the net displacement undergone by the edge of the strongly illuminated gel as a function of time; the evolution locus of the edge point demonstrates the photophobic movement of the gel. Furthermore, local oscillations of the gel, resulting in its periodic swelling and deswelling, give rise to a complex dynamics, such as gradient distributions and multiple illuminated regions. This approach may be helpful in designing intelligent soft robots capable of executing bionic functions.

In conclusion, light can produce opposite photoeffects on the gel movement, depending upon the level and distribution of illumination. In this work, we have succeeded in generating and controlling both photophobic and phototropic movements of BZ gels under patterned spatial illumination. The difference between oscillatory frequencies results in a macroscopic displacement of the photosensitive gel, which moves toward the region of higher frequency. Our experimental results demonstrate that photosensitive BZ gels can be experimentally controlled by manipulating these two photoeffects. Future work will seek to uncover more details about gel movements caused by these opposite effects in more complicated distributions of illumination, such as gradient distributions and multiple illuminated regions. The authors thank Dr Olga Kuksenok and Mr H. Luo for helpful discussions.

Notes and references