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Photonic switching based on the photoinduced birefringence in bacteriorhodopsin films

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Photoinduced birefringence in bacteriorhodopsin films was investigated using pump-probe method and its application for photonic switching explored. A diode-pumped second-harmonic YAG laser was used as a pumping beam and a diode laser at $\lambda = 660$ nm was used as a probing beam. The pump and probe beams overlap at the sample. Without the pumping beam, the probing light cannot transmit the analyzer to the detector. However, due to the photoinduced anisotropy, a portion of the probing light is detected when the pumping beam is present. Since $\lambda = 660$ nm is far from the absorption peak (~ 570 nm) of the ground state, the photoinduced birefringence predominates. Using the intensity-dependent photoinduced birefringence in a bacteriorhodopsin film, we have demonstrated a photonic switch with $\sim 1000:1$ contrast ratio, ~ 0.6 s rise time and ~ 1.5 s decay time. © 2004 American Institute of Physics. [DOI: 10.1063/1.1688456]

Photonic molecular devices have attracted tremendous interests because of their small size and light weight. The biologic protein bacteriorhodopsin (bR) and its derivatives are among the most promising candidates for potential applications in biomolecular photonics due to their unique properties.^{1–3} Bacteriorhodopsin is the light harvesting protein found in the purple membrane of halobacterium halobium and is closely related to the visual pigment rhodopsin. It displays a characteristic broadband absorption profile in the visible spectral region. After absorbing photons, the molecules undergo several structural transformations in a well-defined photocycle. It exhibits a large optical absorption cross section and nonlinearity, ease of optimization and tailoring optical properties, and high stability toward photodegradation and temperature. Bacteriorhodopsin has been proposed for a wide range of applications.^{4–10} Among them, photonic switching has been investigated extensively.^{10–13} Most of the previous works on photonic switching were based on the absorption change of bR after illumination. The wavelength is limited to the absorption peak of the ground Br state at $\lambda = 570$ nm and excited M state at $\lambda = 412$ nm.^{10,12} Moreover, the contrast ratio of such devices is in the 300:1 range, which is inadequate for practical applications.¹⁴

In this letter, we demonstrate a photoactivated switching with good dark state and high contrast at $\lambda = 660$ nm based on the photoinduced birefringence in the bR film. Photoinduced optical anisotropy is one of bR's inherent attributes. It is regarded as a result of the orientation of bacteriorhodopsin molecules in a statistical view. Initially, the bR film is isotropic owing to the random distribution of the anisotropic photosensitive molecules. When the film is illuminated by a linearly polarized light, those bR molecules best aligned along the light polarization direction are bleached while those with

perpendicular orientation are spared, leading to the macroscopic optical anisotropy. Generally speaking, the photoinduced anisotropy contains photoinduced dichroism and photoinduced birefringence. The photoinduced dichroism reaches the maximum when the probing wavelength is around the absorption peak and becomes zero when the probing wavelength is far from the absorption resonance. Here, we investigate the photoinduced anisotropy at $\lambda = 660$ nm, which is far from the absorption resonance of the Br and M states, in order to avoid the photoinduced dichroism and to extend its application toward long wavelengths.

In our experiment, the biological molecules bR were doped in polyvinyl alcohol film. The sample films were purchased from Munich Innovative Biomaterials GmbH (order number WT1N3). Its thickness is ~ 80 μm and optical density is 3 at $\lambda = 570$ nm. Figure 1 shows the experimental apparatus. A diode laser beam with $\lambda = 660$ nm was used to probe the sample. The sample was placed between two crossed polarizers P1 and P2. P1 and P2 are Glan-Thompson polarizers (Edmund Industrial Optics) with 10^6 extinction ratio. A linearly polarized diode-pumped Nd-YAG laser with $\lambda = 532$ nm was used as a pumping beam. A visible broadband quarter-wave plate (Newport 10RP44-1) and a linear

FIG. 1. Experimental apparatus for investigating photoinduced birefringence and photonic switching using a bR film. P₁, P₂, and P₃ are polarizers: P₁ and P₂ are crossed, P₃ is at 45° with respect to P₁.

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FIG. 2. Experimental results before and after the pumping beam is turned on. The inset depicts the photocycle and the corresponding three level transition states.

polarizer P3 were added to the pumping beam path for selecting the desired polarization state. In our experiment, the optical axis of the quarter-wave plate is oriented at 45° with the respect to the polarization direction of the 532 nm laser to transfer linearly polarized light to circularly polarized light. P1 is oriented at 45° with respect to the polarizer P3 in order to obtain maximum phase retardation. As illustrated in Fig. 1, the pumping beam overlaps with the probing beam on the sample.

When the pumping beam is blocked, the probing beam could not reach the detector because the bR film is isotropic. When the pumping beam is turned on, the analyzer P2 transmits some probing light, as shown in Fig. 2. Upon excitation of the initial Br state, the bR molecule goes through several spectroscopically distinguished intermediate states (*K*, *L*, *M*, *N*, and *O*) and relaxes back to the initial state spontaneously.¹⁵ Usually, we may consider only the Br and M states since the lifetimes of other intermediate states in the photocycle are much shorter compared to Br and M states, as shown in the inset of Fig. 2. The initial Br state has an absorption peak at $\lambda = 570$ nm while the long-lived M state has an absorption peak at $\lambda = 412$ nm. The pumping beam wavelength at $\lambda = 532$ nm is close to the absorption peak. Under the exposure to the pumping beam, the bR molecules are selectively excited. Only those bR molecules oriented with their transition dipole moments in or near the polarization direction of the incident beam absorb the light and transit to the excited state M. As a result, the bR molecules exhibit an anisotropic distribution in the illuminated areas. Such an anisotropic distribution rotates the polarization direction of the probing beam. Therefore, a portion of the probing beam transmits through the crossed analyzer. The transmittance of the system can be described by Jones calculus and is given by:⁶

$$T = \frac{1}{2} T_{P1} \left[T_e \exp\left(-j \frac{\Gamma}{2}\right) - T_o \exp\left(j \frac{\Gamma}{2}\right) \right] T_{P2}, \quad (1)$$

where T_{P1} and T_{P2} are the transmittance of the P₁ and P₂ polarizers along their optical axes, and T_e and T_o are the transmittance of the probing beam along the photoinduced extraordinary and ordinary axis, respectively. The photoinduced phase retardation Γ is given by

$$\Gamma = \frac{2\pi d}{\lambda_p} (n_e - n_o), \quad (2)$$

where λ_p is the wavelength of the probing beam; d is the thickness of the film; n_e and n_o are the refractive index corresponding to the film's photoinduced extraordinary and ordinary axes, respectively. Finally, the transmitted probing beam intensity can be obtained by

$$I_t = \frac{1}{4} I_i T_{P1}^2 T_{P2}^2 \left\{ T_e^2 + T_o^2 + 2T_e T_o \left[\sin^2\left(\frac{\Gamma}{2}\right) - \cos^2\left(\frac{\Gamma}{2}\right) \right] \right\}. \quad (3)$$

In Eq. (3), I_i is the incident intensity of the probing beam before the polarizer P₁. From Eq. (3), the transmitted light intensity through the polarizer P₂ is determined by the change in absorption, refractive index, dichroism, and birefringence exhibited in the bR films. Since the dichroism at $\lambda = 660$ nm is almost zero, we can assume that $T_e = T_o = T_{bR}$. Under such a circumstance, Eq. (3) is reduced to

$$I_t = I_b \sin^2\left(\frac{\Gamma}{2}\right), \quad (4)$$

where $I_b = I_i T_{P1}^2 T_{P2}^2 T_{bR}^2$ presents the probing beam intensity after the parallel polarizers P₁ and P₂. Using Eq. (4) and the measured data, we can calculate the photoinduced phase retardation and photoinduced birefringence of the bR film.

Next, we investigate the influence of the pumping and probing beam intensity on the photoinduced birefringence. Results are shown in Fig. 3. Figure 3(a) shows the measured phase retardation of the probing beam as a function of probing beam intensity when the pumping beam was set at $I = 500$ mW/cm². As the probing beam intensity increases, the phase retardation of the probing beam decreases. Although $\lambda = 660$ nm is far away from the resonance absorption of the Br and M states, it still exhibits a small absorption in the Br state. When the probing intensity is weak, only few molecules in the Br state are excited to the M state by absorbing the $\lambda = 660$ nm photons. Most of the molecules in the ground state are bleached to the excited state by the high intensity green pumping beam. As the probe intensity increases, its contribution to the Br state bleaching increases. Since the polarization direction of the probing beam is at 45° relative to the pumping beam polarization, the anisotropic distribution of bR molecules in the film is reduced, leading to the decreased photoinduced anisotropy.

Figure 3(b) shows the phase retardation of the probing beam as a function of pumping beam intensity when the probing beam was set at 5 mW/cm². The phase retardation increases linearly with the pumping beam intensity in the low intensity regime and gradually saturates as the pumping beam intensity gets higher than ~ 500 mW/cm². It is easy to understand this phenomenon. When the pumping beam is weak, the number of the excited molecules is proportional to the intensity of the pumping beam. Certainly, the photoinduced phase retardation is proportional to the pumping beam intensity. However, in the high intensity regime, all the molecules in the ground state have been bleached to the excited state and no more molecules are spared for the increased

FIG. 3. The induced birefringence as a function of pump intensity (a) and probe intensity (b).

pumping beam. As a result, the phase retardation is saturated. The photoinduced birefringence was estimated to be $n_e - n_o \approx 3.2 \times 10^{-4}$.

A photonic switching with high contrast ratio (CR) can be obtained if the pumping intensity is $> 500 \text{ mW/cm}^2$ and the probing intensity is $< 5 \text{ mW/cm}^2$. In our experiment, we achieved $\text{CR} \sim 1000:1$ using 500 mW/cm^2 pumping beam intensity and 5 mW/cm^2 probing beam intensity. As shown in Fig. 2, the photodiode detector has a small thermal noise around the baseline. We have taken the average reading of the noise from the voltmeter while calculating the contrast ratio. High contrast ratio is particularly desirable for photoactivated switching applications.

Figure 4 demonstrates such a photonic switching using our bR film. The response speed is slow due to the long lifetime of the M state ($\sim 10 \text{ s}$). The M-state lifetime can be easily improved by changing the pH value and humidity during fabrication process. From Eqs. (2) and (4), the transmit-

FIG. 4. The measured optical switching results. Pump beam: $\lambda = 532 \text{ nm}$ with $I = 500 \text{ mW/cm}^2$. Probe beam: $\lambda = 660 \text{ nm}$ with $I = 5 \text{ mW/cm}^2$.

tance can be largely enhanced by increasing the film thickness. If the bR film thickness is increased to $d \sim 1 \text{ mm}$, then $\Gamma = \pi$ can be induced and high transmittance obtained.

In conclusion, we have demonstrated a photonic switching using a bacteriorhodopsin polymer film. The device exhibits a $\sim 1000:1$ contrast ratio and the response time is $\sim 0.6 \text{ s}$ due to the long lifetime of the M state. The M-state lifetime can be shortened by changing the pH value and humidity during fabrication process.

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