Protein-based integrated optical switching and modulation

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The static and dynamic response of optical waveguides coated with a thin protein film of bacteriorhodopsin was investigated. The size and kinetics of the light-induced refractive index changes of the adlayer were determined under different conditions of illumination. The results demonstrate the applicability of this protein as an active, programmable nonlinear optical material in all-optical integrated circuits. © *2002 American Institute of Physics.*
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Coupling of optical data-processing devices with microelectronics, as well as sensory functions, is one of the biggest challenges in molecular electronics. Suitable nonlinear optical (NLO) materials with high stability and sensitivity[1] are being intensively researched. In addition to organic and inorganic crystals, biological molecules have also been considered for use in optoelectronics, among which the chromoprotein bacteriorhodopsin (bR) has generated the most interest.[2,3] bR, isolated from the outer cell membrane of the bacterium *Halobacterium salinarum*, is the simplest known ion pump, and one of the best-characterized membrane proteins. Upon illumination it transports protons across the membrane, while undergoing a cyclic series of reactions with quasistable intermediate states (called the photocycle)[4]

$$\mathrm{BR}_{570}\rightarrow K_{620}\rightarrow L_{540}\rightarrow M_{410}\rightarrow N_{550}\rightarrow O_{630}\rightarrow \mathrm{BR}_{570}.$$

The letters denote the ground and intermediate states, and the subscripts refer to the wavelengths/nm of their absorption maxima. The transition rates in dried bR films span from subpicoseconds to seconds. Gels and thin films containing oriented bR molecules[5,6] are extremely stable, maintaining their photoelectric activity for several years at the same level. Despite the large variety of bioelectronic applications utilizing the favorable optical and photoelectric properties of bR and its mutants produced by genetic engineering,[7] no report has yet been published about its application in integrated optics (IO). IO is a discipline of optoelectronics, which integrates various optomodules on a small substrate, in order to create analogs of integrated circuits.[8] Since the theory and measuring techniques for integrated optics are well established, the main limitations in developing devices are of a technical nature, namely, in our case to find the proper NLO material for the particular application envisaged. The Kramers–Kronig relations imply changes in the absorption spectra accompanying changes in the index of refraction. The light-induced change of refractive index of a bR-containing film was indeed demonstrated earlier,[9,10] although not kinetically resolved. This opens the way to a highly interesting use of the NLO characteristics of bR, namely for the modulation of the coupling of light into and out of IO devices controlled by the light-induced transitions of bR.

In our experiments bacteriorhodopsin-containing purple membranes were suspended in distilled water and dry bR films of good optical quality were produced by layering the suspension on a smooth surface. Integrated optical experiments were carried out using slab geometry waveguides (Microvacuum Ltd, Budapest). The waveguide consisted of a thin $\mathrm{Si(Ti)O_2}$ layer (refractive index $n_F \approx 1.8$, thickness $d_F \approx 200$ nm) on a 16×48 mm glass substrate (refractive index $n_S \approx 1.5$) surface. Coupling of light into the waveguide was achieved through a grating formed in the waveguide (line density: $1/\Lambda = 2400\ \mathrm{mm}^{-1}$, length of the grating region: 1 mm). In a thin waveguide, only the zeroth transverse electric (TE) and transverse magnetic light modes can propagate.[11,12] Since the guided modes have a significant evanescent component, coupling to or from an external beam is strongly influenced by the refractive index of the material above the grating area (the adlayer). Thus, a change of the index of refraction of bR (Δn_A) will modulate the angle α of incoupling.

Angular dependence of coupling of a plane polarized light from a He–Ne laser (Melles Griot, 15 mW, $\lambda = 632.8$ nm) into the waveguide was measured when the grating region was covered by bR (see Fig. 1). We determined the changes of the incoupling angle during the bR photocycle initiated by a pulse from an excimer laser pumped dye laser (Lambda Physik Lextra 100, Rhodamine 6G, $\lambda = 580$ nm, $E = 10$ mJ/pulse) or from a Nd: Yttrium–aluminum–garnet laser (Continuum) equipped with a tunable

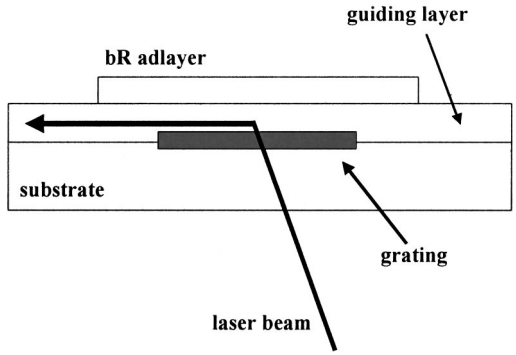

FIG. 1. The grating coupler with a bacteriorhodopsin adlayer. Incoupling is schematically indicated.

optical parametric oscillator head ($\lambda = 410$ nm, 10 mJ pulse energy).

The waveguide was placed on a rotational stage (Ealing Electro Optics Digital Positioning System), by which the coupling angle α could be controlled to an accuracy of 10^{-4} deg. The incoupled light was measured at the ends of the waveguide by a photomultiplier (Hamamatsu). The light intensity signal was amplified by a laboratory-built preamplifier and then recorded with a Le Croy 9310L transient digitizer. In order to improve the signal to noise ratio, the time resolution of the system was limited by low-pass filtering to 0.8 μs.

From the angular shift of the peaks of incoupling (compared to the case when no bR adlayer is present), the refractive index of the (unexcited) bR adlayer was determined to be to 1.52, in agreement with previous observations by other methods.[9,10] Furthermore, those experiments have shown that under continuous illumination the refractive index changes to an extent consistent with a buildup of the population of the intermediate *M*. Such changes in the adlayer refractive index should correspondingly shift the positions of the incoupling peaks, as illustrated in Fig. 2. Consequently, within certain angular ranges, the intensity of the incoupled light should change during the bR to *M* transition, thus yielding the sought-for modulation or switching driven by external light. In order to prove this hypothesis, we performed kinetical experiments. The rotational stage was stopped at different angles in the region of effective coupling and the

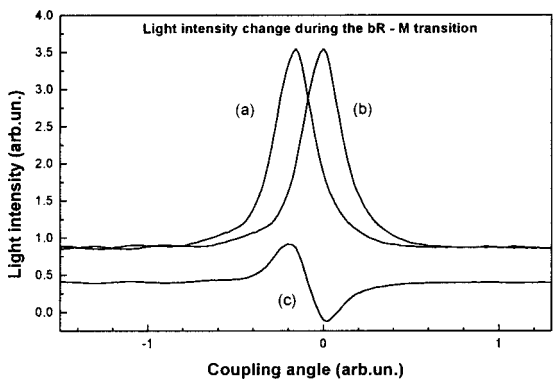

FIG. 2. An illustration of the principle of the switching. The angular dependence of coupling with the *M* form (a) and with the bR ground state (b) are calculated from the known refractive index change. The lower curve (c) represents the expected changes of the intensity of coupled light during the bR to *M* transition.

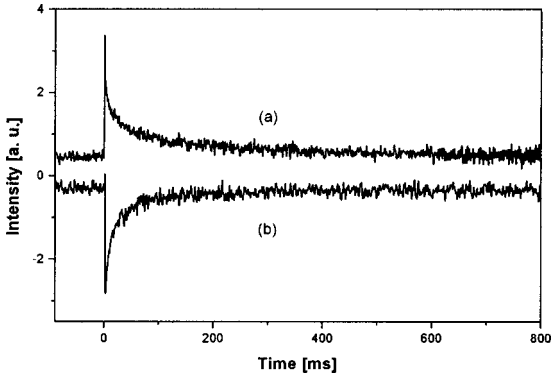

FIG. 3. Coupled light intensity changes measured upon flash excitation of the film. Ground state bR was excited by 570 nm flashes. The measuring light intensity was attenuated to 0.5 mW (He–Ne laser, $\lambda = 633$ nm), so as to avoid considerable pre-excitation of the sample. Traces were recorded at two positions [(a) and (b), with incoupling angles $\theta_a = 5.967°$ and $\theta_b = 6.167°$], on opposite sides of the incoupling peak at TE mode ($\theta_{TE} = 6.067°$). The amplitude of the relative light intensity change at θ_a was about 70%.

light intensity changes following flash excitation were measured.

Figure 3 shows two traces measured at opposite sides of the incoupling peak corresponding to the TE mode. The traces were analyzed using global fitting with multiexponential curves. In the millisecond domain two exponentials resulted in a good fit, with time onstants $\tau_1 = 57$ ms and $\tau_2 = 350$ ms, characteristic of the second half of the photocycle (*M* decay) at low humidity.[13] The antisymmetry of the traces show that the primary origin of the intensity change is a transient change of the coupling angle, confirming the dominating role of refractive index changes in the observed switching effect. From the maximal value of the angular shift, the corresponding light-induced refractive index change of the adlayer was calculated (2×10^{-3}) using the waveguide equations.[12] Its value is close to previous findings.[9,14] To be able to correlate the changes of the coupling geometry to the steps of the photocycle, we also performed absorption kinetic experiments on the same sample under identical conditions. Evaluating the kinetics of the *M* intermediate (obtained by measuring absorption changes of the bR film at 405 nm upon light excitation), we obtained the same time constants as mentioned above. The correlation is in agreement with the Kramers–Kronig origin of the observed refractive index changes on this time scale, corresponding to the nearly 160 nm difference between the absorption maxima of the bR ground and *M* states. The speed of light modulation based on this effect, therefore, should be limited by the kinetics of the *M* formation to about 50 μs in the photocycle of wild type bR, when using flash excitation.[13] Under continuous illumination, however, when the light density is much lower, the buildup of the *M* population τ_M, and consequently the refractive index changes are limited by the light intensity and the decay rate of *M*, typically to the millisecond time regime. With a 10 mW/mm^2 illumination from a He–Ne laser, $\tau_M \approx 15$ ms (data not shown).

A faster switch can be devised by making use of the photoreaction of the *M* intermediate: it is known that blue light shortcuts the photocycle, driving the *M* form back to the ground state.[15] Optical changes accompanying this process

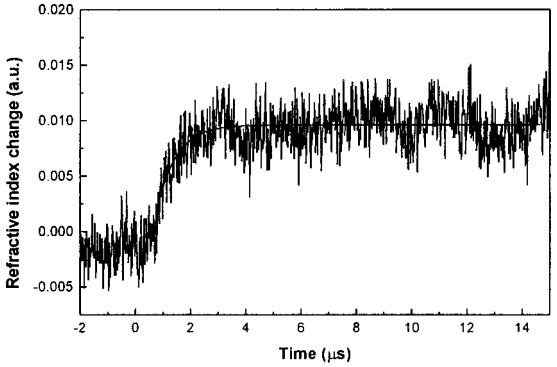

FIG. 4. Demonstration of the fast switch. The sample was preilluminated with a 10 mW beam of a He–Ne laser, and after a 1 s adaptation period the accumulated *M* state was driven back by a short (10 ns) blue flash ($\lambda = 410$ nm, 10 mJ pulse energy). Incoupling was tuned to one of the inflection points of the TE peak measured with continuous illumination ($\theta = 6.146°$), in order to maximize the light intensity change.

occur in the submicrosecond range. Figure 4 shows the kinetics of light intensity changes measured after a blue flash superimposed on red background illumination. The speed of optical switching is characterized by a submicrosecond rate constant (0.8 μs, instrument limited), while the corresponding refractive index change is nearly the same as that associated with the forward reaction, but with opposite sign (-1.8×10^{-3}).

The above results demonstrate the feasibility of using a protein as a programmable active element in integrated optical devices. Hence the fabrication of microstructured all-optical devices coated with bR adlayer is primarily a technological task. The size, speed, and cyclicity of the light-induced refractive index changes of bR are comparable to or exceed the corresponding properties of inorganic NLO crystals, while the possibility of genetically controlling the optical properties of bR (absorption spectrum, cycle time, etc.)[7] offers a great and unique versatility for optical circuit design.

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