Biooptical computing and molecular optoelectronics

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Introduction

Molecular electronics and biocomputing has hitherto mainly concentrated upon the electron as the mobile information carrier. In parallel with the development of optoelectronics and optical computing, one can also envisage the emergence of molecular optoelectronics and biooptical computing, in which the photon is the mobile element. The scope for exploiting optical biomolecules in optical information processing devices is likely to be far more extensive than the potential range of electron-based devices, since there are far more natural molecular assemblies responding to photons compared with the number of those involving electrons. Even some comparatively lowly single-celled organisms have molecular machinery enabling them to respond to light,[1] and most multicellular creatures have some form of eye, whereas electric organs are essentially restricted to a few species of fish. Here we exclude the electrically charged ion; bionic devices comprise the central and peripheral nervous systems possessed by all multicellular animals.

Although one may envisage three-dimensional structures based on biological molecules capable of optically-directed information processing (one example of which has already been demonstrated in the laboratory, viz. a block of bacteriorhodopsin used as an optically addressable memory), this short article is restricted to devices in which the optically responsive biomolecules are deposited on optical waveguides.

[1] Sineshchekov, O.A. et al. Rhodopsin-mediated photoreception in cryptophyte flagellates. Biophys J. (2005) doi: 10.1529/biophys j. 105.070920.

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Elements of integrated optics

An optical waveguide is a thin slab of high refractive index material surrounded by lower refractive index material.[2] Once introduced into such a structure, light remains confined within it and propagates with a phase velocity whose value depends on the refractive indices and thicknesses of the slab and its surrounds. The guided wave is a standing wave within the high refractive index slab, and an evanescent wave without, decaying exponentially away from the interface. The full electromagnetic field distribution can be found by solving Maxwell's equations for a multislab structure.[3] The solutions to the equations are discrete, corresponding to different modes $m = 0, 1, 2, ...$, each characterized by an effective refractive index $N_{\rho,m}$, where ρ is the polarization (either transverse electric (TE), with field components H_x, H_z and E_y (where x is the direction of propagation and z the direction perpendicular to the surface of the high refractive index slab) or transverse magnetic (TM), with field components E_x, E_z and H_y). The effective refractive index N is simply the ratio of the velocity *in vacuo* to the phase velocity in the waveguide. Since the N depend on the refractive index and thickness of an adlayer of molecules present on the surface of the high refractive index slab F, modulation of these molecules by chemical or optical means can form the basis of amplification and gating devices.

An optically-switched optical switching device is typically constructed by depositing a layer, denoted A, of photoactive material on top of the core waveguiding layer F. An important parameter describing the potential performance of a refractive index switch is the coefficient $\partial N/\partial n_A$, summarizing the way in which (optically-induced) changes in the refractive index of the adlayer A affect the effective refractive index of the entire structure. This coefficient depends on all the optogeometric parameters of the waveguide.[4] One of the main aims of the designer is to optimize this coefficient for a given application. A powerful approach to enhancing it is by using multislab structures for the F-layer.[5]

The grating coupler

The grating coupler is a highly convenient but not indispensible component in integrated optics devices, especially fledgling computing ones. It enables an external (freely

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[2] 'Thin' typically means of nanometric dimensions. The cutoff thickness, below which no wave can be guided, is given by $\lambda \arctan [(n_F / n_C)^{2\rho} a^{1/2}]/[2\pi(n_F^2 - n_S^2)]$, where λ is the wavelength of the light *in vacuo*, the n are the refractive indices of the high refractive index material (F) and the cover (C) and support (S) surrounding it, $a = (n_S^2 - n_C^2)/(n_F^2 - n_S^2)$ is the asymmetry parameter, and $\rho = 0$ or 1 represents polarization.

[3] Tien, P.K. Integrated optics and new wave phenomena in optical waveguides. *Rev. mod. Phys.* **49** (1977) 361–420; Ramsden, J.J. Review of new experimental methods for investigating random sequential adsorption. *J. statist. Phys.* **73** (1993) 853–877.

[4] Ramsden, J.J. Sensitivity enhancement of integrated-optics sensors using Langmuir-Blodgett lipid films. *Sensors Actuators* B **15–16** (1993) 439–442.

[5] Nesnidal, R.C. & Walker, T.G. Multilayer dielectric structure for enhancement of evanescent waves. *Appl. Opt.* **35** (1996) 2226–2229.

propagating) beam to excite an internal one, i.e. a guided mode, under precisely defined conditions.[6] Working as an incoupler, a specific mode is excited when the external beam is incident onto the grating at a particular angle α; the same mode will generate an external beam leaving the grating at that angle, in which case the grating works as an outcoupler. Gratings can be created by either topographical or refractive index modulation.

Measurement of these angles α offers a very sensitive route to determining the effective refractive indices N, and this effect has already been exploited for chemical and biochemical sensing purposes.[7] It is easy to see how a chemically actuated switch could be set up: a grating coupler coated with a monolayer of molecules is tuned such that an external beam incident onto the grating at a fixed angle excites a guided mode that is collected by a photodetector at the end of the waveguide. Upon exposing the device to a second molecular species, which binds to and changes the conformation of the first one, the effective refractive index changes such that the coupling condition:

$$N = n_{\text{ext}} \sin \alpha + \ell\lambda/\Lambda \tag{1}$$

(where n_{ext} is the refractive index of the external medium, (typically air) ℓ is the diffraction order, λ is as before the wavelength of the light *in vacuo*, and Λ is the grating constant) is no longer satisfied, and the light reaching the detector is extinguished. Proteins containing heavy metal centres are attractive candidates as molecules for coating the grating coupler (constituting the A layer), since conformational changes, which may be triggered by slight changes in the composition of the ambient atmosphere, can result in significant shifts in the visible absorption spectrum. If the guided light is chosen such that its wavelength is in a region of enhanced anomalous dispersion, very large refractive index shifts may result.

Another possibility, attractive for building up switching networks, is to trigger conformational changes in the molecules constituting the A layer by a light pulse applied normally to the waveguide. An optically triggered switching effect has been recently demonstrated in bacteriorhodopsin,[8] which is known to undergo significant refractive index changes during its photocycle,[9] the sequence of absorption spectrum changes triggered by an actinic light pulse.[10] Since the photocycle follows a very well defined time course, sophisticated synchronization between different switches should be possible. Moreover, the velocity and other attributes of the cycle can be influenced in predetermined ways

[6] Tiefenthaler, K. & Lukosz, W. Sensitivity of grating couplers as integrated-optical chemical sensors. *J. opt. Soc. Am.* B **6** (1989) 209–220.

[7] Ramsden, J.J. Optical biosensors. *J. molec. Recognition* **10** (1997) 109–120.

[8] Ormos, P., Fábián, L., Oroszi, L., Wolff, E.K., Ramsden, J.J. & Dér, A. Protein-based integrated optical switching and modulation. *Appl. Phys. Lett.* **80** (2002) 4060–4062.

[9] Tkachenko, N.V., Savransky, V.V. & Sharonov, A.Yu. Timeresolved refractive index change during the bacteriorhodopsin photocycle. *Eur. Biophys. J.* **17** (1989) 131–136.

[10] Xie, A.H., Nagle, J.F. & Lozier, R.H. Flash spectroscopy of purple membranes. *Biophys. J.* **51** (1987) 627–635.

by selecting the chemical environment of the molecule, or by making amino acid substitutions in the polypeptide chain surrounding the chromophore.

Dimensions of the device

Typical grating couplers are 1–2 mm wide and have grating constants Λ of a few hundred nm. They are usually incorporated in waveguiding films F about 150 nm thick (supported on optical glass 0.5 mm thick) with a refractive index of 1.7–1.8. The overall dimensions of the waveguide are about 1 cm wide and anything from a few mm to a few cm long, and the actual diameter of the external beam in the incoupling configuration is about 0.8 mm. Therefore several milliard molecules are involved in triggering. Little effort has so far been devoted to further miniaturizing such optical switches.

Organometallic complexes as molecular optoelectronic components

Although proteins are certainly attractive candidates for light addressable refractive index modulators, it is not so easy to modify the native form to enhance prespecified attributes, and they can certainly not be designed from scratch at present. On the other hand, interesting optical properties are possessed by many large organometallic complexes, which can be designed and synthesized according to known rules. A desirable goal in this field is to assemble designer complexes on the surfaces of optical waveguides, capable of carrying out sophisticated photonic processing. We are only at the very beginning of the road leading to this goal, however, and the first step is to understand how such molecules spontaneously assemble at the solid-liquid interface, i.e. when a solution of them is brought into contact with an optical waveguide. Here, optical waveguide lightmode spectroscopy (OWLS) has turned out to be very useful as a high precision technique with which the optogeometrical parameters of the deposited layer can be followed *in situ* during assembly with excellent time resolution. Analysis of the deposition kinetics has revealed that the orientation of the deposited molecules is strongly dependent on the bulk concentration of the solution.[11]

Ultimately, it may even be possible to assemble diffractive and other structures at a waveguide surface by letting molecules spontaneously organize themselves. That such molecular assembly is possible in principle is hinted at by the very complex diffractive structures found on certain butterfly wings and responsible for their intensely iridescent colours; under the microscope these structures are revealed as a wonderland of intricacy.[12] The evidence so far suggests that they are

[11] Constable, E.C., Harverson, P. & Ramsden, J.J. Adsorption of ruthenadendrimers to silica–titania surfaces studied by optical waveguide lightmode spectroscopy (OWLS). *J. Chem. Soc. Chem. Comm.* (1997) 1683–1684.

[12] Ghiradella, H. Light and color on the wing: structural colors in butterflies and moths. *Appl. Opt.* **30** (1991) 3492–3500; Ghiradella, H. Structure of butterfly scales: patterning in an insect cuticle. *Microscopy Res. Technique* **27** (1994) 429–438.

too complex for a spontaneous self assembly process, but rather are "grown": the assembly is under genetic control.

In this very brief survey, current research and anticipated trends have been covered. Waveguides are now well understood; the next significant advance is likely to result from the incorporation of adaptive complex materials, as typified by bacteriorhodopsin (bR). This is an extraordinarily robust protein, and attempts to use other photoactive proteins have so far foundered on their extreme fragility, hence the interest in synthesizing advanced artifical materials of comparable functional sophistication.