

## All-optical switching in the near infrared with bacteriorhodopsin-coated microcavities

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Photoinduced molecular transitions in bacteriorhodopsin are used to reversibly configure a micron-scale photonic component in which the optical response is resonantly enhanced. The chromophore retinal undergoes photoinduced all-*trans* to 13-*cis* conformational change, which tunes resonances in a silica microsphere coated with three bacteriorhodopsin monolayers. The tunable, all-optical resonant coupler reroutes a near-infrared beam ( $\lambda_{\text{probe}} \cong 1311$  nm) between two tapered optical fibers using a low-power ( $<200$   $\mu\text{W}$ ) green pump ( $\lambda_{\text{pump}}=532$  nm). The approach represents a bottom-up paradigm for fabrication of hybrid molecular-photonic architectures that employ self-assembled biomolecules for optical manipulation at small scales. © 2006 American Institute of Physics. [DOI: 10.1063/1.2372711]

The long-standing goal of photonics is to effectively manipulate light with light alone while keeping the device dimensions small. To this end, a great deal of effort has been spent on identifying materials with a strong optical response and developing micron-scale dispersive and resonant components which amplify light-matter interaction when the material response is weak. The conventional approach has been to exploit nonlinearities of the established photonic materials to control propagation of optical signals with intense laser pulses.<sup>1-3</sup> In parallel with these developments, several biomaterials have been explored for photonic applications.<sup>4,5</sup> In particular, the photochromic protein bacteriorhodopsin<sup>6</sup> (bR) stands out as a prominent candidate for fabrication of future biomolecular photonic devices. Its photoresponse has been optimized by evolution, which promises reliable device performance with high quantum yields and fatigue resistance. It is equally important that the protein forms highly organized membrane assemblies that can be readily crafted onto surfaces,<sup>7,8</sup> e.g., of photonic components. Due to its unique optical properties bR has been investigated extensively for optical storage,<sup>9</sup> signal delay,<sup>10</sup> signal processing,<sup>5</sup> and switching.<sup>11-14</sup> Various all-optical switching schemes based on the absorption shift,<sup>11</sup> induced anisotropy,<sup>12,13</sup> and changes of the refractive index<sup>14</sup> have been demonstrated in the visible band, yet none of these techniques can be extended into the telecom band (1311/1550 nm) where bR is virtually transparent. However, we find that high- $Q$  resonant components can be readily employed to cover longer wavelengths. Our experiments show that optical microresonators are sensitive to small induced dipole changes in ultrathin, optically dilute molecular monolayers even when these changes occur at wavelengths far from any absorption band. In this letter we investigate a near-infrared all-optical photonic switch based on photoinduced isomerization of bR adsorbed on the surface of a high- $Q$  silica microsphere. We introduce fabrication of optical components by self-assembly of biological macromolecular aggregates onto micron-scale photonic platforms. This approach represents a general bottom-up paradigm for hybrid molecular-photonic devices employing molecules to perform photonic functions.

Photoexcitation of bR triggers a complex photocycle that involves isomerization of the retinal chromophore.<sup>6</sup> Illumination around 568 nm changes the conformation of the retinal from the all-*trans*, 15-*anti* protonated Schiff base, found in the thermodynamically stable ground state, to the 13-*cis*, 15-*anti* deprotonated isomer prevalent in the metastable  $M$  state. The  $M$  state relaxes spontaneously into the ground state through several intermediaries, which complete the photocycle. The availability of genetically modified bR mutants with a prolonged  $M$ -state lifetime such as D96N ensures complete conversion between the two states. Isomerization alters the optical properties of bR, which perturb the frequency of interacting resonant modes. Whispering-gallery modes (WGMs) in optical microcavities can significantly enhance the interaction of the evanescent optical field with the material, conveying it as a resonant frequency shift. According to the analytical result of the first-order perturbation theory the wavelength shift of a microsphere resonance upon isomerization is proportional to the change of molecular polarizability and the surface density of the adsorbed molecules, and inversely proportional to the cavity size.<sup>15</sup> With the retinal surface density of  $9.12 \times 10^{12}$   $\text{cm}^{-2}$  and the photoinduced polarizability change ( $\Delta\alpha$ ) of several hundreds of atomic units,<sup>16,17</sup> high- $Q$  ( $Q \sim 10^5$ ) silica microspheres are exceptionally sensitive to  $\Delta\alpha$  in ultrathin molecular layers. This makes them ideal for all-optical switching applications.

A 300  $\mu\text{m}$  silica microsphere ( $Q \sim 2 \times 10^6$ ) was formed by melting the tip of a single mode optical fiber in a butane-nitrous oxide flame. Three layers of bR mutant D96N were adsorbed onto the microsphere surface using alternate electrostatic deposition of cationic poly(dimethyldiallyl)ammonium chloride (PDAC) and anionic bR membranes.<sup>7,8</sup> In each cycle, a single oriented ( $\sim 55$  Å thick) PDAC/bR monolayer was self-assembled onto the microcavity surface<sup>7</sup> [Fig. 1(a)]. The bR adsorption process slightly degraded the microcavity  $Q$  to  $\sim 5 \times 10^5$ , which we believe was caused by the introduction of scattering impurities during each drying process. Two parallel, single mode optical fibers held 250  $\mu\text{m}$  apart in a standard 1 cm acid-resistant polystyrene cuvette were tapered by hydrofluoric acid erosion.<sup>18</sup> Once etched, the fibers were immersed in 0.01M phosphate buffered saline with  $\text{pH}=7.4$ . The bR-coated microsphere was

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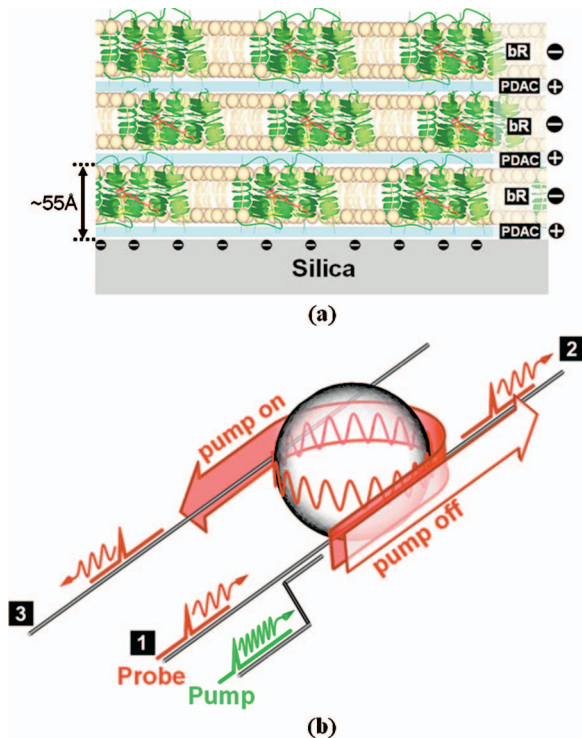


FIG. 1. (Color) (a) Schematic of three oriented PDAC/bR layers adsorbed by alternate electrostatic deposition onto the surface of silica microsphere. Cytoplasmic surface of bR is at the bottom and extracellular at the top of the lipid bilayer. Seven transmembrane  $\alpha$ -helices (green) surround the optically active chromophore retinal (red). (b) Schematic representation of an all-optical switch operation. A silica microsphere with adsorbed three layers of D96N is positioned between two optical fibers forming a tunable four-port resonant coupler. A green pump laser ( $\lambda = 532$  nm), connected to input port 1, controls the conformational state of the retinal. When the pump is off (all-*trans* isomer) the near-IR probe is transmitted from input port 1 to output port 2 as indicated with the straight arrow. Turning the pump on (13-*cis* isomer) reroutes the probe into output port 3 (red arrow).

then spring loaded between the two tapered fibers, as shown in Fig. 1(b). Resonant modes were excited with a distributed feedback laser, operating around 1311 nm, connected to port 1. To determine the resonant wavelength, the modulation current was scanned periodically at 100 Hz with a sawtooth shaped function. Photodiodes connected to fiber ports 2 and 3 were used to monitor the transmitted intensity of the probe and a spectrum containing 1000 points was recorded every  $\sim 200$  ms with a LABVIEW program. Polynomial fitting algorithms were used to determine the resonant wavelengths from the parabolic minimum (port 2) or maximum (port 3) fits to the resonant peak.

The silica microcavity positioned between two tapered fibers serves as a four-port tunable resonant coupler [Fig. 1(b)]. The switching of a fiber-coupled IR source (port 1) between the two output ports (2 and 3) is photoinduced, activated with a fiber-coupled green pump laser which controls the conformational state of the adsorbed bR. The molecularly functionalized microcavity thus redirects the flow of near-IR light between two optical fibers. The switching results are summarized in Fig. 2. Photomicrographs in Fig. 2(a) show the top view of the coupler obtained with a conventional charge-coupled device (CCD) camera (top) and the corresponding IR images showing the flow of the probe beam (bottom). With the pump off, the probing light from input port 1 is detuned from resonance and is directly transmitted into the output port 2 [Fig. 2(a): C]. The corresponding reso-

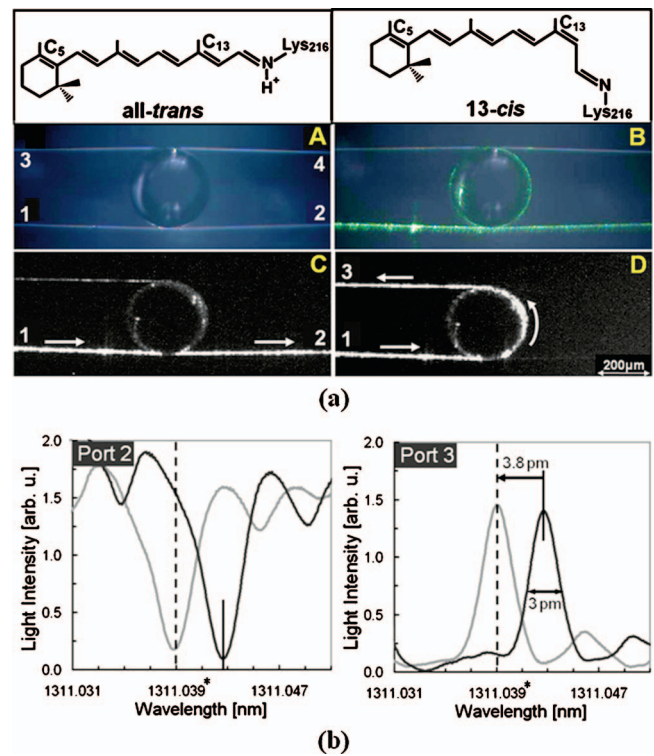


FIG. 2. (Color) (a) (A) Top-view photomicrograph of a bR-coated microsphere positioned between two tapered fibers. The image was obtained at ambient illumination with a CCD camera. (B) The same microsphere with whispering-gallery resonances excited with a green pump beam from port 1. (C) IR image of 1311 nm probe beam propagation with the pump turned off and (D) IR-probe propagation with the pump on. The corresponding conformational states of the retinal are shown above the photomicrographs. (b) Resonant transmission spectra of a microsphere measured in ports 2 (left) and 3 (right) by scanning the probe laser around  $\lambda^* = 1311.039$  nm. With the pump off (black line) port 2 shows a high transmission and port 3 a low transmission at  $\lambda^*$ . The reverse is true when the pump is on (gray line).

nances, acquired in port 2 (resonant trough) and port 3 (resonant peak) by scanning the IR probe around the probing wavelength ( $\lambda^* = 1311.039$  nm), indicate high transmission at  $\lambda^*$  through port 2 and low transmission through port 3 [Fig. 2(b)]. The reverse is true when the pump beam is turned on. The pump evanescently excites WGMs propagating around the microsphere's equator, inducing bR photoisomerization along their path. A low-power green cw laser ( $< 200$   $\mu$ W at 532 nm) is sufficient for this purpose as its effective absorption is resonantly enhanced. Isomerization reduces the retinal polarizability, tuning the peak/trough of the resonance to match the wavelength of the IR probe which is then rerouted into the output port 3 [Fig. 2(a): D].

Isomerization of a single monolayer shifts the resonance by  $\sim \frac{2}{3}$  of its full width at half maximum. The shift is proportional to the surface density of the retinals<sup>15</sup> and therefore can be enhanced by controlled layering of several oriented membranes.<sup>7,8</sup> For the case at hand the switching contrast is maximized with three bR monolayers, the photoisomerization of which shifts the resonance close to the midpoint between its original position and that of the nearest neighbor as shown in Fig. 2(b). The transmission spectra in the figure indicate an extinction of  $-9.4$  dB in port 2 and a 9.8 dB increase in transmission in port 3. Significantly better switching performance is theoretically possible with critically coupled adiabatic tapers<sup>19</sup> or by using optical microcavities

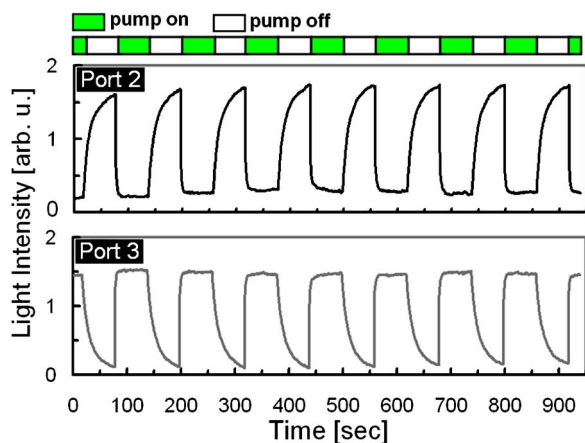


FIG. 3. (a) Switching kinetics for periodic pump modulation measured in ports 2 and 3. The time-resolved transmitted intensity of the probe reflects a fast photoinduced transition of bR from the ground (all-*trans*) to the *M* state (13-*cis*) followed by a slow ( $\tau_{\Delta} \sim 11$  s) thermal recovery of the ground state.

with lower resonant mode densities such as microtoroids<sup>20</sup> or microring resonators.<sup>1</sup>

The switching dynamics is dictated by the speed of the bR photochromic transitions. Time-resolved switching data for periodic pump modulation are presented in Fig. 3. The traces reveal a fast transient time scale associated with the phototransformation from the ground state to the *M* state and a slow thermal ground state recovery  $\tau_{\Delta} \sim 11$  s. Faster switching can be achieved with ultrafast photochromic systems such as diarylethenes,<sup>21</sup> in which case the speed is limited by the cavity photon lifetime.

To summarize, we have demonstrated a tunable all-optical resonant coupler using a high-*Q* silica microcavity coated with ultrathin molecular layers. The switch operates far from the molecular absorption bands, which allows it to

modulate near-infrared probe beams with a low-intensity visible pump.

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