

What this work demonstrates is that it is possible to supply power to devices fabricated on silicon that are moved out of the plane of the wafer using polymer actuators. (Of course, this technology is not limited to silicon, but can be used with glass, quartz, or other substrates.) The possible applications are exciting, because so many different kinds of electronic, optical, and micromechanical devices can be produced on silicon. One can envision moving light-emitting diodes or semiconductor lasers, for example, or a comb-drive microgripper being moved into position to grasp a small object.

A particular application we are pursuing is a chip for the study of living cells or single-celled organisms. A cavity etched in silicon with a sealable lid could be used to capture a cell, and both the cavity floor and the lid could carry devices for measuring a property of interest. For example, there could be electrodes on them so that the resistance could be measured or a potential applied. Alternatively, a light source on the lid could be coupled with a light detector on the floor for optical measurements. Chemical sensors could monitor the response of the cell. A wafer could be covered with thousands of these devices so that information could be gathered from a great many cells. The devices presented in this paper are one step on the way to such goals.

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- [31] The 3000 Å thick Al layer was sputtered in an Ar flow of 20 L/min at a pressure of 2 mtorr using a voltage of 380 V (a current of 360 mA) for 20–25 min. The RIE parameters were: 10 sccm/min CHF₃, 100 sccm/min SF₆, and 10 sccm/min O₂ at 250 W and 150 mtorr.
- [32] The following conditions were used: 293 sccm/min He, 968 sccm/min N₂O, and 57 sccm/min SiH₄ at 21 W and 900 mtorr; substrate heated to 350 °C; 40 min.
- [33] A 30 Å thick adhesion layer of Cr followed by a 1000 Å layer of Au; pressure <10⁻⁶ torr, 4–5 Å/s deposition rate for Au.

Photochemical Micromachining of Lysozyme Crystals**

By Orlin D. Velev,* Eric W. Kaler, and Abraham M. Lenhoff

Self-assembled ordered matrices of biological macromolecules are novel nanostructured materials that could find applications in catalysts, in biosensors, or in data storage devices.^[1,2] Three-dimensional protein crystals are a little-studied class of such materials. This is surprising as they are readily available, since crystals are routinely obtained during protein characterization and purification.^[3,4] By virtue of the well-defined and compact structure of the protein molecules, and their efficient functionality, for example, as enzymes or in electron-transfer systems, such 3D protein lattices hold promise for efficient biocatalysis and high-density memory storage. Protein crystals, however, grow in a variety of shapes and sizes, and they may have value in materials synthesis only if it is possible to control and manipulate their sizes and/or shapes. This cannot be done by mechanical machining as the crystals are extremely fragile (they incorporate 30–80 vol.-% of water and the molecules in the lattice are bound together only by weak intermolecular forces^[4]). As an alternative, we have developed ways to micromachine crystals of the protein lysozyme using light.

The original lysozyme crystals, in the hydrated state, are transparent and stable under UV-vis illumination. In principle, it may be possible to drill or cut them by the application of energy from a powerful laser, but the thermal and mechanical stresses produced are likely to break and destroy the crystals. Instead, our novel approach exploits the properties of crystals infused with fluorescent surfactants; these can be manipulated photochemically and photophysically by the light beam in a fluorescent microscope. Here

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we first present the basics of the process of infusing the crystals with a fluorescent surfactant, and then describe the effects of the photochemical degradation of lysozyme following irradiation of pyrene-infused crystals. A complementary phenomenon is then presented, wherein protein deposition or removal occurs photophysically during the illumination of the crystals in collimated light beams. Finally, we show an example of photochemical etching and drilling.

Infusion of the Crystals with Fluorophores: Fluorophores can either be incorporated during crystal growth, or be adsorbed and penetrate into previously formed crystals. The fluorescence probes used were the amphiphilic pyrene derivatives listed in the Experimental section. To characterize surfactant mass transfer within crystalline protein matrices, we have studied the infusion process by quantitative fluorescence microscopy.^[5] The effective fluorophore diffusion coefficients range from $2\text{--}30 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, depending on the type of pyrene derivative. After the crystal had become saturated, over a period of 24–48 h, the adsorbed fluorophores were uniformly distributed throughout the lattice. The slow infusion is a consequence of the strong surfactant adsorption on the protein molecules (estimated to be 10–12 *kT*).

When a high-intensity light beam is focused through the microscope objective onto the surface of a saturated crystal, the pyrenes in the illuminated area gradually photobleach to non-fluorescent compounds. This facilitates fluorescence recovery after photobleaching (FRAP) experiments,^[6] in which the evolution of the darker bleached spot on the fluorescent crystal is followed in time (Fig. 1a). The difference in intensity between the bleached spot and the surrounding area, and the sharpness of the boundary, remains largely unchanged for as long as 72 h, which demonstrates the absence of exchange between the bleached and unbleached surfactant. This indicates that the self-diffusion coefficient of the adsorbed surfactant is negligibly low and that although the pyrene derivatives are not chemically bound to the host protein molecules, they are effectively immobilized in the crystal lattice.

Photochemical Denaturation and Etching: The first photochemical effect observed in the presence of the pyrenes is the denaturation of the irradiated protein. Anomalous results were obtained in the FRAP experiments when attempts to

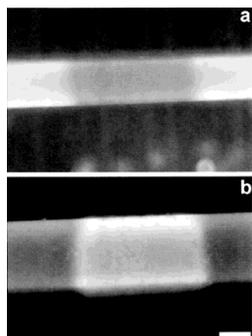


Fig. 1. Two different results of photobleaching experiments on lysozyme crystals infused with Pyr-SO₃H. a) A fully saturated crystal shows ordinary photobleaching. b) A partially saturated crystal exhibits photoactivation. The picture was taken 30 min after the bleaching and traces of etching in progress can be seen (to the left, top, and bottom of the bright area). Scale bar = 50 μm .

bleach infused crystals were conducted at short times (3–6 h) after the start of fluorophore infusion. Instead of the formation of a darker spot, as described above, the bleaching procedure created a spot brighter than the uniformly fluorescent area outside the bleached domain (Fig. 1b). Subsequent observations of these photoactivated crystals showed that the crystal surfaces in the irradiated area begin to erode within a few minutes. This etching process is complete within about 24 h. Micromanipulation of such crystals allows the observation of all four sides of the irradiated area (Fig. 2) and shows that the crystal has been nearly uniformly etched to a depth of approximately 10 μm . The etched patterns in Figure 2 appear to represent a snapshot of the position of the surfactant diffusion fronts at the moment of photoactivation.

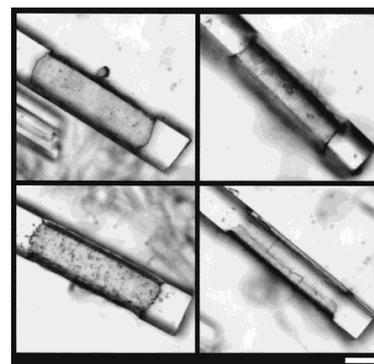


Fig. 2. Micrographs of a photoactivated and etched crystal partially infused with Pyr-C₃-COOH. The crystal has been turned by mechanical manipulation to reveal all four sides around the etched area. Scale bar = 50 μm .

Figure 3 outlines our hypothesis concerning the molecular origins of the observed photoactivation and etching.

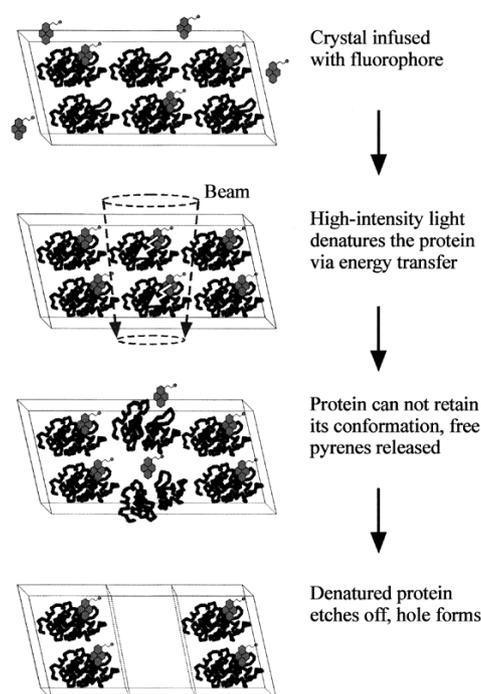


Fig. 3. Schematic presentation of the photochemical denaturation processes underlying crystal micromachining.

The strong adsorption of the pyrene amphiphiles is likely to be accompanied by energy transfer to the host protein molecules and quenching of the pyrene fluorescence. Subsequently, at higher excitation intensities the protein may be photochemically degraded by the excess energy transferred from the fluorophore. This would result in protein denaturation and the release of free pyrene (which is unquenched, hence the increase in fluorescence intensity seen in Fig. 1b). The denatured protein is unable to remain crystalline and redissolves from the surface. This hypothesis is consistent with the data of Kumar et al.,^[7] who demonstrated that appropriately designed pyrene derivatives can be used as photochemical “scissors” to split lysozyme molecules into well-defined fragments. They reported that the photochemical interaction between the pyrenes, cobalt(III) hexamine, and lysozyme led to photocleavage at the boundary of the tryptophan-108 amino acid residue. This was accompanied by degradation of this and other tryptophan residues (which are the most photochemically active residues of the protein molecule and the ones expected to participate in energy transfer^[8]).

To prove further that photochemical denaturation and photoactivation are active in these systems, we studied the fluorescence spectra of solutions of pyrene butanoic acid (Pyr-C₃-COOH) in the presence of lysozyme. The emission spectrum of pure Pyr-C₃-COOH reproduced that of the monomer emission reported in the literature.^[9] After lysozyme was added to the solution, the spectrum remained unchanged in shape, but the intensity decreased by about 50 % within 30 min and by 90 % in 7 h. Thus, after a comparatively long period of protein-fluorophore interaction, the pyrene emission became strongly quenched by the protein. The slow timescale of quenching may be attributed to the gradual adsorption, re-configuration, and eventual penetration of the pyrene moiety into the hydrophobic core of the lysozyme. After bleaching the intensity approximately doubles. This increase is consistent with the photoactivation of the bleached areas (Fig. 1b) and can be explained by degradation of the protein-pyrene complex and the resulting partial release of free pyrene (Fig. 3). Similar patterns were observed in the excitation spectrum. The protein denaturation hypothesis is also supported by the observation that a fine precipitate of possibly denatured protein appeared in the cuvette after the bleaching.

Such photochemical denaturation can be exploited to drill microscopic holes through lysozyme crystals. A very thin UV beam (ca. 30 μm), shaped by a pinhole aperture in the microscope illuminator, was focused on the surface of crystals infused with Pyr-C₃-COOH. Following an exposure period of 30 min or more, the crystals appeared initially to be largely intact, but over a period of up to 24 h a hole formed in the area that had been irradiated. Such holes typically do not penetrate the whole crystal, and it was difficult to estimate the exposure time needed to form them (overexposure led to bleaching of the surfactant and adverse results). An improved procedure is outlined below.

Protein Deposition and Removal in a Collimated Beam: The etching/drilling phenomena described above result from lysozyme photochemical degradation, and are slowly manifested after irradiation of the crystal. However, we also observed that illumination of the crystal in the collimated beam of the microscope can itself lead to protein deposition or removal not caused by photochemical denaturation. In this respect it is important to realize that the light beam from the illuminator is converging above the focal plane and diverging below it. Accumulation and deposition of protein was observed in the converging beam when the microscope was focused on the top facet of the crystal. Conversely, the disassembly of the degraded protein in the bleached crystal is enhanced below the focal plane of the objective, that is, in the path of a diverging light beam.

This behavior is broadly analogous to the manipulation of colloidal particles^[10] and polymer molecules^[11] in collimated laser beams. However, the phenomenon is not driven by the transfer of light momentum directly to the protein molecules, as it is encountered only in systems where *both* protein and fluorophore are present. On the other hand, the same behavior is seen in systems containing another fluorophore, BODIPY-C₄-COOH, which is activated in the visible region without bleaching or denaturation of infused crystals. Thus, the phenomenon is not coupled to the photochemical reactions between the pyrene derivatives and the lysozyme and may result either from direct photon pressure, or from effects such as inelastic scattering and/or colloidal thermophoresis. The effect is easily reproducible and could also be used for directional protein deposition and micromachining. An example of how a converging light beam can be used for controlled deposition of protein is given in Figure 4, where the metamorphosis of a crystal illuminated by such a beam is shown. At short times the crystal is deformed and flattened against the underlying glass substrate as if the beam exerts some pressure on its surface (second frame in Fig. 4). At longer times an additional mass of amorphous protein is deposited within the spot of the converging beam (third and fourth frames in Fig. 4).

Finally, we combined the two complementary phenomena into a controlled procedure for crystal drilling. The crystal is processed in cycles of 10 min irradiation (during which the protein is both denatured and redissolved from the bottom of the crystal) followed by 10 min of rest (to allow time for the disassembly of the denatured protein). The hole forms and expands in the converging beam from the lower face up to the upper crystal surface. The hole size and quality are monitored in transmitted low-intensity illumination during the rest cycles. A completely drilled-through crystal with a hole with clean, mostly cylindrical, walls can be obtained by applying about 10 cycles (Fig. 5).

In summary, we have found two complementary effects caused by the interaction of UV and visible light with lysozyme crystals infused with fluorescent surfactants, which can be used for light-driven manipulation of protein arrays.

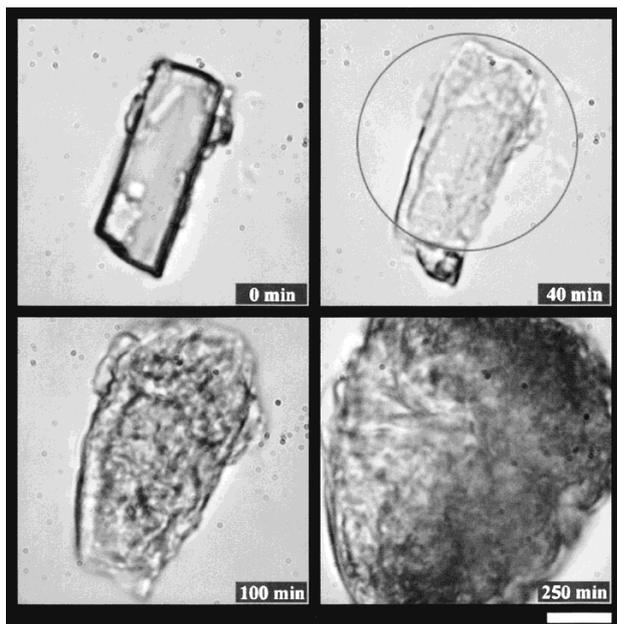


Fig. 4. Four consecutive frames demonstrating the flattening of a crystal on the surface and additional deposition of protein under the action of the fluorophore-mediated light pressure effect. The fluorescent substance used, BODIPY-C₄-COOH, is excited in the visible region and does not show photobleaching or quenching in the presence of lysozyme. The shaded circle in the second frame marks the approximate boundary of the focused beam. Scale bar = 50 μm .

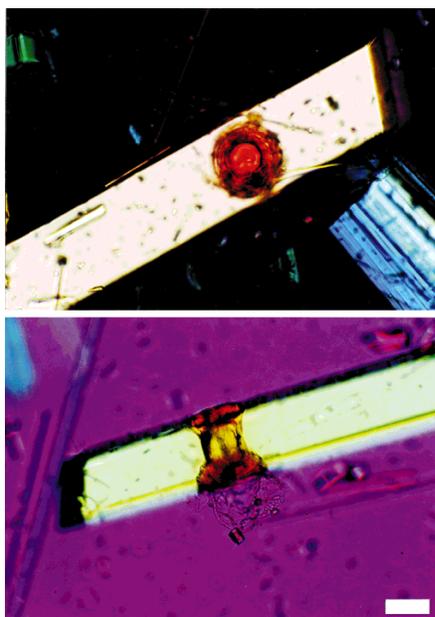


Fig. 5. Photographs in polarized light of a crystal that has been photochemically drilled via partial infusion with Pyr-C₃-COOH, and cyclic exposure to a thin beam of UV light. The lower frame was taken through the side of the crystal to show that it is completely penetrated by the hole. Scale bar = 50 μm .

The first is the photochemical degradation of lysozyme in the presence of pyrene, where the denatured protein subsequently dissolves and is etched off the crystal. The second is a phenomenon where the protein phase can be deposited, moved, or dissolved by collimated light beams. Both of these methods could find application in the optical micro-

maching of protein crystals such as etching, drilling, cutting, patterning, or directed deposition onto substrates. This photochemical approach can also be applied to patterning and micromachining of other protein systems such as layers and hydrogels adsorbed or immobilized on sensors and biochips. Light-triggered bleaching or photoactivation, such as shown in Figure 1, could be used for recording information in the lattice. In general, we believe that fluorophore-infused protein crystals or layers have yet-to-be realized potential as precursors for advanced materials.

Experimental

Lysozyme was obtained from Sigma (Prod. No. L-6876). All solutions were adjusted to pH 10 and contained 0.3 M NaCl, 3×10^{-4} M citrate buffer, and 10 mg mL^{-1} Na₃. The protein concentration before crystallization was 15 mg mL^{-1} . The crystals were grown by a batch method, in which the protein solutions were left for 3–14 days at 22 °C in closed glass or plastic vials. The fluorescent compounds were supplied by Molecular Probes (USA) and were used without further purification. Two of the fluorescent markers were 1-pyrene derivatives: pyrene butanoic acid (denoted here as Pyr-C₃-COOH) and sodium pyrene sulfonate (Pyr-SO₃H). An alternative fluorophore was a fluorescent-labeled fatty acid, BODIPY-C₄-COOH (Prod. No. D-3834), which is excited in the visible range (475–500 nm). All of these fluorophores have rather low, but not negligible, solubility and thus are able to diffuse slowly through the aqueous medium to saturate the protein crystals.

The experimental samples were encapsulated in 1 mm thick Probe-clip imaging chambers from Sigma. The chambers were sealed by a thin layer of fluorinated grease (Krytox, DuPont, USA), which was applied between the silicone rubber surface and the cover glass. A few droplets of the lysozyme solutions, along with a few suspended crystals, were transferred by sterile pipette to the chamber. A minute amount of the crystalline fluorescent substance (≈ 0.1 – 0.5 mg L^{-1} of crystalline suspension) was gently scattered in the solution. The samples were immediately sealed from above with 0.17 mm thick microscope cover slips and transferred onto the microscope stage for observation.

The fluorescence experiments were carried out using an Olympus BH-2 microscope equipped with a 100 W stabilized mercury burner. The samples were excited in the 334–365 nm range and the light emitted above 410 nm collected and analyzed. The digital images were collected by a cooled charge coupled device (CCD) camera (Star-1, Photometrics, Inc.) and transferred to a Macintosh computer for frame processing.

Typically, the observations were carried out through a 10–40 \times objective with a fully closed aperture diaphragm and a neutral density attenuator in the illuminator path. A large, uniformly shaped protein crystal was selected, centered, and focused in transmitted illumination. The bleaching of the spots shown in Figure 1 was carried out through a 20 \times , 0.40 NA (numerical aperture) objective with a fully closed field diaphragm, a semi-opened aperture diaphragm, and no attenuator. The narrow beams used for drilling (Fig. 4) were produced through a high-magnification, long-working distance (40 \times , 0.55 NA) objective, a custom-made field diaphragm with an opening of 0.25 mm, and no attenuator.

The fluorescence spectra were recorded on an SLM 8100 spectrofluorimeter (SLM Aminco, USA). The samples were contained in tightly capped 1 cm path length quartz cuvettes. The emission spectrum of the pure saturated fluorophore solution was collected during excitation at 340 nm, and the excitation spectrum was recorded for the fluorescence intensity at 410 nm. 10 mg mL^{-1} lysozyme were then added to the saturated Pyr-C₃-COOH solution and the spectra were followed over time for up to 7 h. After this the cuvette holding the solution was irradiated for 20 min in the light path of the microscope (with the objective removed) and re-examined by spectrofluorimetry. All spectra, obtained in 2–4 successive emission or excitation scans, were stable and reproducible.

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Narrow Bandwidth Luminescence from Blends with Energy Transfer from Semiconducting Conjugated Polymers to Europium Complexes**

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Semiconducting (conjugated) polymers have several properties that are advantageous for photonic applications:

they have high fluorescence efficiencies (>60 %), emit at wavelengths that span the entire visible spectrum, are mechanically flexible, and can be deposited as uniform thin films by casting from solution. Since the fabrication of the first polymer light-emitting diode (LED) in 1990,^[1] there has been extensive research on polymer LEDs and many improvements have been made.^[2–4] Single-color displays fabricated with arrays of polymer LEDs will soon be commercially available. Full color displays will require pure red, green, and blue emission.

Obtaining pure emission colors from conjugated polymers or small organic molecules is difficult because their emission spectra typically have a full width at half maximum (FWHM) of 50–200 nm. Efficient, pure red-emitting polymer LEDs are particularly hard to make because the human eye is more sensitive to orange emission than red; if the spectrum falls even slightly in the orange, the perceived color is “orangish red”. Red LEDs can be made by filtering out orange emission or by using polymers or dyes whose emission starts in the red and extends into the infrared, but these LEDs are inefficient because only part of their emission is useful. In contrast to organic chromophores, rare earth ions have very sharp emission spectra (FWHM < 4 nm).^[5] In this paper we show that pure red emission can be achieved in polymer LEDs by transferring energy from blue-emitting conjugated polymers to europium complexes. Similar methods have been used to make red LEDs from small organic molecules.^[6–10] We show that blends of Eu complexes in poly[2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene] (CN-PPP) have an emission spectral line-width (FWHM) of only 3.5 nm, a photoluminescence (PL) efficiency of 27 %, and an electroluminescence (EL) efficiency of 1.1 %. These blends could be useful as a source of pure red light for full color displays or for photonic devices that require monochromatic light.

To incorporate Eu³⁺ into conjugated polymers, we synthesized a family of soluble Eu complexes with β -diketonate ligands, codissolved the complexes and polymers in a solvent, and cast films. We chose β -diketonate ligands because they sensitize Eu³⁺ emission.^[5,11] The sensitization process is as follows: the ligand absorbs energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to the Eu³⁺ ion.^[12,13] Thus, the first design rule for making fluorescent Eu complexes is that the triplet level of the ligand must be higher in energy than the emissive level (⁵D₀) of Eu³⁺. A second design rule is imposed by the need for energy transfer from the polymer to the rare earth complex. In order to transfer energy from a conjugated polymer to the ligands of a Eu complex by dipole coupling (Förster transfer), the emission spectrum of the polymer and the absorption spectrum of the ligand must overlap.^[14,15] Since the ligands whose triplet level lies above the ⁵D₀ level of Eu³⁺ absorb in the ultraviolet or blue region of the spectrum, we chose CN-PPP as the host polymer; CN-PPP is a blue-emitting polymer that has been used to make LEDs that emit at wavelengths as low as 385 nm.^[16] We

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