

Deforming Materials With Light: Photoresponsive Materials Muscle In On the Action**

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actuators · molecular machines ·
photo-responsive materials

Pound for pound muscle packs a real punch with a performance that exceeds engines and motors of a similar size. Given this observation, it's perhaps no surprise that making an artificial muscle of equivalent output to natural muscle is a huge challenge that has so far eluded researchers. An artificial muscle generating around 100 W kg^{-1} with a response time of less than a second and an energy conversion efficiency of 30% or so would be very nice. Add in silent operation, 10 million or more operating cycles, self-repair and self-sensing and then we would be getting closer to muscle. Finally, we would want to be able to fabricate these systems from microelectromechanical systems (MEMS) to macroscopic actuators for humanoid robots (and a vast array of applications in between). In some respects, different types of artificial muscles can mimic most of these muscle functions, albeit with less sophisticated structures. However, the combination of all these functions into a single material remains the greatest challenge.

At the “heart” of muscle action is the chemically fuelled sliding filament process causing the sarcomeres in muscle fibers to contract. This essential motor unit of muscle is replicated many times in series and parallel arrangements to generate useful forces and movement. Many researchers believe that the development of improved artificial muscles should also replicate this same design strategy. Indeed, there are many examples of molecular machines—molecules that change shape or size on demand—that could fulfil this role.^[1] Much recent focus has been to assemble these individual motor molecules into arrays that can work cooperatively so that the movements and force accumulate and generate larger movements. For example, DNA strands^[2] or rotaxane molecules^[3] have been assembled as monolayers on a flexible cantilever such that conformational changes caused the microscopic cantilever to reversibly bend. Here the action

of individual molecules has been upscaled to the micro-dimension.

In a recent breakthrough, Inoue and co-workers have demonstrated how to self-assemble molecular machine elements such that they cooperatively produce a sliding function that resembles, in a primitive way, the filament sliding mechanism of muscle.^[4] By using a simple procedure, they prepared a layered hybrid coating consisting of inorganic postassium hexaniobate nanosheets (1.23 nm thick) intercalated by ion exchange with a polyfluoroalkyl azobenzene cationic surfactant (abbreviated as C3F-Azo). X-ray diffraction and atomic force microscopy revealed that the intercalated C3F-Azo molecules were nearly close-packed at a stacking angle of 43° within the interlayer spaces (Figure 1). 84-layer films were prepared on a glass surface and a sharp scalpel cut was made to reveal the film edge. Exposure to ultraviolet light (365 nm) caused the azo unit in the C3F-Azo molecules to isomerize from the *trans* to *cis* form resulting in a hinge-like deformation of the individual molecules. The cooperative motion of the close-packed bilayer of C3F-Azo within the hexaniobate interlayers resulted in a sliding motion of adjacent niobate nanosheets. The deformed structure was stable after UV treatment but could be reverted to the original shape by visible-light irradiation (435 nm) that induced the reverse *cis* to *trans* azo isomerization. The total reversible sideways shift of the multilayer hybrid sheet was 1500 nm or nearly 18 nm per layer. We do not know the total length of the active hybrid film so it is not possible to determine the dimensional change as a percentage of the initial length, but it is relevant to note that individual sarcomeres in muscle generate only ca. 250 nm length contraction from a starting length of 2–3 μm . By proper assembly, these small movements accumulate to generate the very large contractions of many millimeters produced by muscle tissue. In a similar way, Inoue and co-workers have convinced azo-containing molecules to assemble and cooperate so that their individual shape changes are coordinated in the one direction. Hopefully, these hybrid films can be soon removed from their glass substrate to generate linear contractions and useful work.

Muscle fibers are not always straight and muscle contraction is not always linear. Some of the muscle fibers in an elephant's trunk, for example, are helically wound in concentric cylinders.^[5] Contraction of these fibers can cause a rotating action. Other fibers run longitudinally, producing

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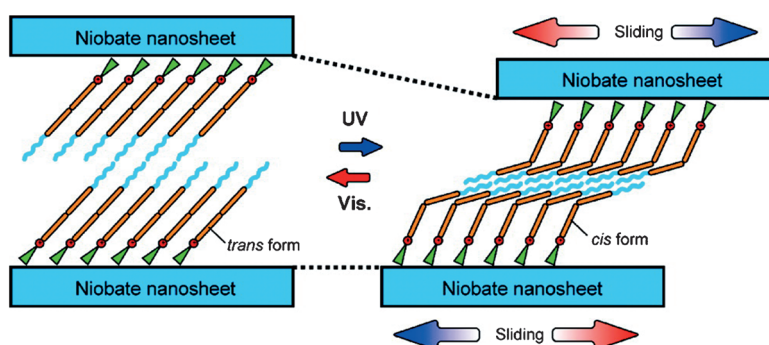


Figure 1. Illustration of the intercalated layered structure of stacked azobenzene molecules within niobate nanosheets and their reversible sliding motion. (Reprinted with permission from Inoue et al.^[4] Copyright 2011 American Chemical Society.)

bending. With these arrangements, the contraction of selected muscle fibers generates the enormously complex range of motions and incredible dexterity of the elephant appendage. Similar structures exist in tentacles, tongues, and worm bodies. In a highly simplified imitation, we have been able to assemble helically wound carbon nanotubes into yarn fibers that produce large and fast rotating, or torsional, actuation when electrically stimulated.^[6] The helical nature of the twisted carbon nanotubes that make up the yarn fibres generate a torsional motion due to partial untwisting when the yarn swells as a result of electrochemical charging. A light-actuated twisting motion has also been recently reported by Bardeen and co-workers.^[7] Here a UV-initiated dimerization reaction between adjacent 9-anthracenecarboxylic acid molecules in a crystalline microribbon generates interfacial tension between reacted and non-reacted regions that drives a shape change leading to a twisting of long, thin ribbons (Figure 2). The twisting was reversed when the light source was removed as a result of the thermally driven reverse chemical reaction. Complex twisting and bending of azobenzene liquid crystal polymer networks have also recently been observed by White and co-workers.^[8] Here strips of the glassy polymers were illuminated with polarized light such that the direction of bending/twisting by controlling the direction of the liquid crystal alignment within the films.

These examples highlight some of the recent progress in forming light-actuated artificial muscles. While impressive, there is much work still to do before we have truly biomimetic artificial muscle systems powered by light irradiation. In

particular, the field would benefit from demonstrations of photoactuators performing real mechanical work. It is quite common to report the shape change induced by irradiation in which the actuator material is free to move without external loads. In real applications, however, the actuator must work against an external load and here the net actuation is the sum of the deformation caused by the light stimulus and the normal elastic deformation caused by a change in the external stress. The extent of elastic deformation is determined by the actuator material's Young's modulus. In the simplest linear systems the actuator strain (percent elongation based on the starting length) decreases with increasing applied stress at a rate inversely proportional to the modulus. The maximum stress generated is called the blocking stress and corresponds to the stress needed to prevent any actuation strain. The work output is usually a maximum when a stress equal to one half of the blocking stress is applied to the material, demonstrating that optimal performance can only be achieved by matching the actuator to the expected load. Some recent attempts to quantitatively model light-induced actuation^[9] are helpful, but experimental validation is needed. Producing a useful artificial muscle is not simply a case of generating movement, regardless of how large or how fast. The further development of photoresponsive materials as useful artificial muscles will no doubt continue to proceed through innovative chemistry and nanoassembly, but hopefully, also by generating quantitative information regarding work capacities, power output, and overall energy-conversion efficiencies.

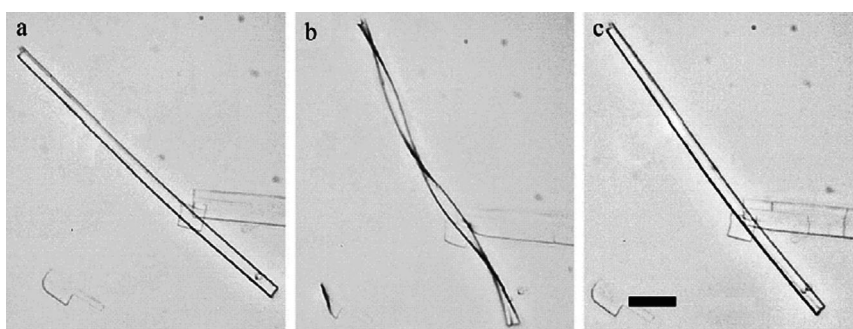


Figure 2. Optical microscopy images (scale bar 20 μm) showing the twisting of a single microribbon as a result of UV light exposure. Images show the ribbon a) before, b) during, and c) after irradiation. (Reprinted from Ref. [6]. Copyright 2011 American Chemical Society.)

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