Optical Pendulum Generator Based on Photomechanical Liquid-Crystalline Actuators

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Ⓢ Supporting Information

ABSTRACT: For converting light energy into electricity, an optical pendulum generator was designed by combining photomechanical movement of liquid-crystalline actuator (LCA) with Faraday's law of electromagnetic induction. Bilayer cantilever actuators were first fabricated with LDPE and LCA. Their photomechanical movement drove the attached copper coils to cut magnetic line of force generating electricity. The output electricity was proportional to the changing rate of the magnetic flux, which was greatly influenced by light intensity, film thickness, and sample size. Continuous electrical output was also achieved. This simple strategy may expand applications of photoactive materials in the capture and storage of light energy.

KEYWORDS: optical pendulum generator, electromagnetic induction, liquid-crystalline actuator, photoactive materials, photomechanical materials
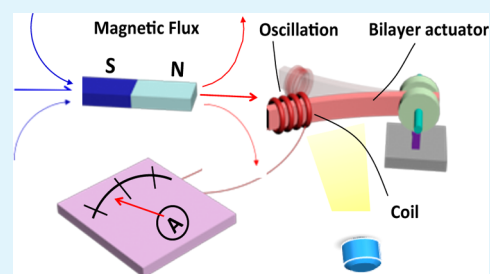
1. INTRODUCTION

Functional materials in response to external stimuli, such as thermal,[1] electric,[2] light,[3] and pH,[4] have attracted much attention because of their potential applications as actuators for biomedical and mechanical purposes. Among these stimuli, light is so special that it is one of clean energy, supplying one noncontact way to control actuation rapidly, precisely, and remotely.[5] Generally, photoresponsive materials are one of the keys to obtaining remote control of actuating behaviors. Being one of the most famous light-active materials, azobenzene-containing polymers often show an interesting photomechanical effect, converting light energy into mechanical stress by the macroscopic deformation of polymers.[6] Several discontinuous motions such as bending, twisting, or contraction have been reported for azobenzene-containing actuator films upon UV-light irradiation.[7,8] However, it often needs exposure to light with other wavelengths to restore the films from their bent or twisted deformation.[9]

Very recently, oscillatory motion of a photoresponsive cantilever was reported by using identical light exposure from two sides of the polymer film.[10,11] This provides feasibility to undergo a continuous output of mechanical energy, which could be suitable for fabrication of light-energy transducing device. Despite a amount of researches have been dedicated to investigating the actuation of photoactive materials, the application of actuators still remains limited due to only mechanical energy being outputted.[5,12,13] One of the exceptions is coupling the photomechanical energy into electric power. For instance, piezoelectric polyvinylidene fluoride (PVDF) laminate composites were fabricated by using a rotating beam chopper

generating periodical light exposure on an azobenzene actuator film. Then photoinduced deformation of the photoactive film exerted stress on the PVDF films, generating piezoelectric voltages.[14,15] Generally, most of the grid electricity has been generated at power station by electromechanical generators, which converts mechanical energy into electrical energy via the Faraday's law of electromagnetic induction. The source of mechanical energy may be a reciprocating or turbine steam engine, through a nuclear reaction, water falling, wind turbine, combustion engine, or any other source of energy. In various systems, macroscopic light-driven mechanical energy has been achieved on photoactive azobenzene materials as exposed to light energy. Thus, it is greatly desirable to convert the optical-mechanical energy into electricity through the electromechanical generators. In this paper, we report an optical pendulum generator (OPG) based on photoactive materials coupling output the photomechanical into electricity. To fulfill the energy transducing, we fabricated a cantilever of liquid-crystalline actuator (LCA) by casting azobenzene liquid-crystalline polymer on a grooved low-density polyethylene (LDPE) substrate, the cantilever showed a fast and strong bending and unbending upon UV-light exposure on and off. When attaching copper coils onto one free end of the cantilever and setting them under a magnetic field, an alternating current was then generated when the cantilever swung upon light exposure on. To the best of our knowledge, this is the first

attempt to construct a light-driven electromechanical generator using photomechanical azobenzene polymers. This simple and highly efficient mechanical coupling strategy may expand the applications of photoactive materials in capture and storage of light energy.

2. EXPERIMENTAL SECTION

Fabricating the Bilayer Film. First, one commercialized LDPE film (20 μm, thickness) was carefully polished with silicon carbide sandpaper (1000 grit) in one direction. Second, the LDPE film was sonically washed in deionized water and dried in nitrogen. Third, one photoactive polymer solution (10 wt % in THF) was cast onto the polished LDPE substrates. Then, the bilayer film was obtained upon annealing in an oven at 40 °C for 24 h. For measurement, the film was cut into samples with various aspect ratios. The light irradiation was exposed using a UV-LED with an intensity of about 13.2 mW/cm^2.

Fabrication of OPG. The generator was fabricated by mounting induction coils on one free end of the bilayer film (25 mm × 10 mm × 0.04 mm), which was then set in a magnetic field of a Horseshoe-shaped (magnetic flux density of 850 Guass) or a ring-shaped permanent magnet (magnetic flux density of 1200 Guass) or rare earth magnet (NdFeB & SmCo, 100 mm × 50 mm × 20 mm, magnetic flux density of 9100 Guass). Multiple turn coils (14 mm in diameter, 2 mm in height, 132.8 Ohm of the static state electric resistance) were wound by enamel-insulated copper wire (the wire diameter is 0.01 mm). The open-circuit voltages were measured by the Agilent 34411a multimeter, which was directly connected to the two ends of the coils without introducing any external loads in the circuit. For contrasting the damping effect, the coils were connected with a load resistor of about 1100 Ohms.

3. RESULTS AND DISCUSSION

The photoactive liquid-crystalline elastomer (LCE) was synthesized according to a previously reported method.[9] The chemical structure of the monomer and the cross-linker are illustrated in Figure 1. Here, one rigid azobenzene cross-linker without any spacer was used and the adopted monomer has one side-chain mesogen terminated with a strong polar group on the phenyl ring, expecting for acquiring a fast thermally restored back isomerization of azobenzene groups in the
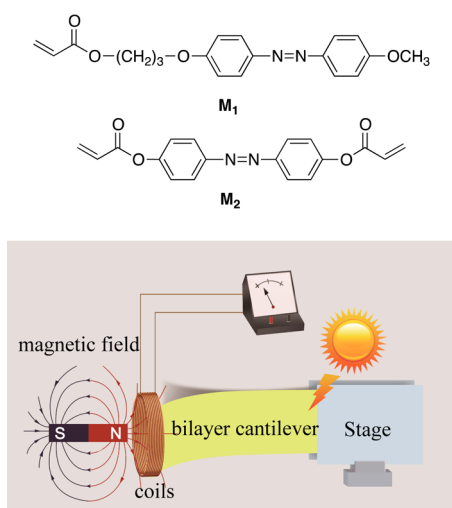

Figure 1. Chemical structures of the azobenzene monomer and azobenzene cross-linker used for synthesizing the photoactive polymer (above), and scheme illustrating the fabrication of the optical pendulum generator. Copper coils were fixed on one end of the bilayer film, cutting the magnetic line of force to generate electricity under a magnetic field (below).

chemically linked polymer network.[16] The LCE polymer showed a glass-transition temperature at about 57 °C, and the DSC curve also exhibited a broad endothermic peak at about 200 °C, which was assigned to the liquid crystal to isotropic (LC−I) phase transition. The typical Schlieren texture of the nematic (N) phase was observed at slow cooling down a film sample from 200 °C to room temperature. The UV−vis absorption spectra demonstrate that the synthesized polymer exhibited a rapid trans to cis photoisomerization upon exposure to UV light (Figure S6a in the Supporting Information) and a fast cis to trans back isomerization in dark (Figure S6b in the Supporting Information),[17] which makes it suitable for continuously and effectively coupling the light energy into electricity upon photoirradiation.

A bilayer cantilever (Figure S4 in the Supporting Information) was fabricated by casting the solution of the LCE polymer onto LDPE film. To obtain fast photoinduced bending-unbending motion of the actuator film,[12] typical methods have been reported by using a thin photoactive polymer film stuck on LDPE substrate.[6] The photoactive film with monodomain aligned mesogens was prepared by polymerization of liquid-crystalline mixtures of azobenzene-containing monomers and cross-linkers in a cell precoated with rubbed polyimide films as alignment layers. Here, we adopted one simple strategy to align azobenzene groups on the supported LDPE film. The LDPE surface was just prescratched to produce microgrooves, acting as the alignment layers to induced alignment of the deposited azobenzene polymer.[18] Upon solvent evaporation and thermal annealing, a bilayer film was obtained with homogeneously aligned mesogens along the groove direction. Polarizing optical microscopic (POM) images confirm the mesogenic alignment of the photoactive film (Figure S5 and S6 in the Supporting Information).[19] The fabricated bilayer film exhibited good flexibility and mechanical properties contrasting to one single photoactive layer film or reported laminated bilayer films.[20−22]

Upon UV irradiation, the bilayer film exhibited fast photoinduced bending and unbending behaviors. As shown in Figure S7 in the Supporting Information, one bilayer film (25 mm × 10 mm × 0.04 mm) bent toward the light source when it was irradiated from the photoactive polymer side, and then it unbent back after the light was turned off. This is similar to the photomechanical behavior of azobenzene-containing LCE films with monodomain aligned mesogens.[9] Upon photoirradiation, the photoactive polymer layer contracted by the trans−cis isomerization and phase transition of the aligned mesogens, while the supported LDPE layer is photo inert. This resulted in an anisotropic contraction of the whole film along the grooved direction (Figure S8 in the Supporting Information), enabling it bent like a "bimetal" way.[9,23] The rapid reverting to the initial flat state in dark should be due to fast cis−trans isomerization (Figure S9 in the Supporting Information), leading to the expansion of the photoactive layer and then the unbending of the whole film. Opto-mechanical experiments on the bilayer film showed reverse behaviors of photoinduced stress, as shown in Figure S10 in the Supporting Information. Fast growth of the stress toward a photostationary equilibrium state was observed from 0.01 to 2.7 MPa when the sample was irradiated with UV-light. Turning light off, the reverse process of releasing the stress was observed. From the viewpoints of energy saving, this fast restore (unbending) of the bilayer film in dark shows advantageous over other LCEs with reverse unbending motions
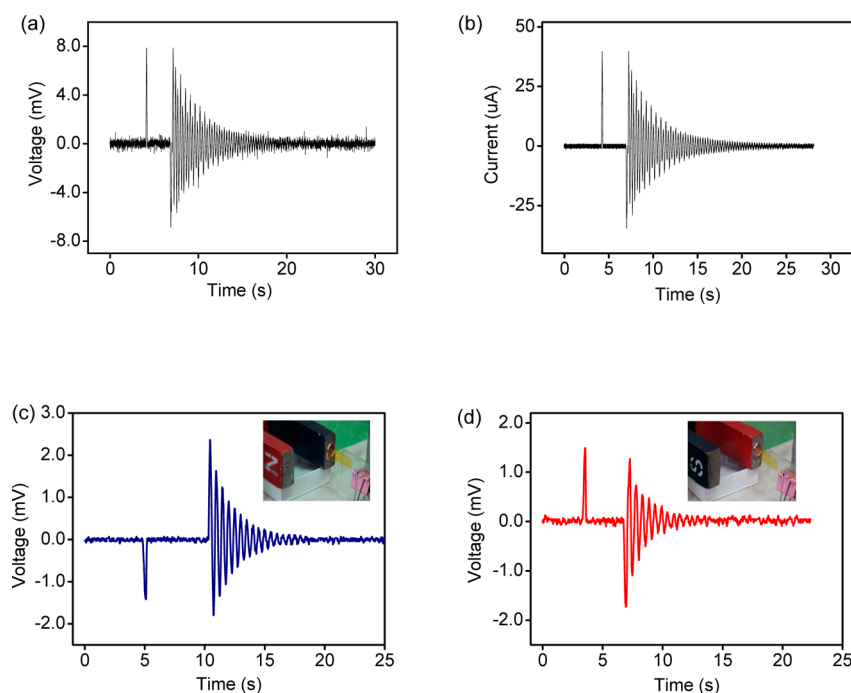
Figure 2. (a) Induction voltage and (b) current upon UV-light exposure triggered the bilayer film bending and unbending when the light was turn off. (c, d) A set of inverted induction voltage was generated when the coils were placed to the reversed magnetic flux flow (inset figures show the coils were erected under a reversed magnetic field).

by using another visible light incident,[6] because no light energy was needed in the present system.

To further convert the photoinduced mechanical energy into electricity, an innovative mechanical coupling was designed by mounting copper coils on the far end and then the bilayer film was set into a magnetic field constituting an OPG, as shown in Figure 1 (also in the Experimental Section of the Supporting Information). As shown in Figure 2a, b, the bilayer film bent and simultaneously brought the motion of the copper coils when UV light was illuminated (Movie S1 in the Supporting Information). Induction voltage (current) was generated due to the change of magnetic flu when the coils passed through the magnetic field according to the Faraday's law of electromagnetic induction. When light was turned off, the bilayer film unbent back and also drove the motion of the coils in the magnetic field. Consequently, a corresponding reverse voltage (current) was generated accompanying this unbending motion. Oscillate voltage was observed after the bilayer film reverted to its original position. As shown in Figure 2c, d, changing the direction of magnetic flux produced an inverted induction voltage and current pulses, indicating that the measured induction signals were generated by the motion of the copper coils on the bilayer film under the magnetic field rather than the error of measurement system.

Electrical measurement demonstrated that the output electricity of the photodriven bilayer film was proportional to the changing rate of the flux through the coils. The light intensity, film thickness and sample size exhibited strong influence on the swing rate of the coils. As shown in Figure 3 and Table 1, prolonging the irradiation time resulted in the change of the bending velocity and the value of the induction voltages. When prolonging the exposure time form 1s to 4s, it was observed that the OPG output an identical bending voltage of about −1.1 mV but an increasing max voltage from 0.9 mV to 2.2 mV. Increasing the irradiation time also resulted in the
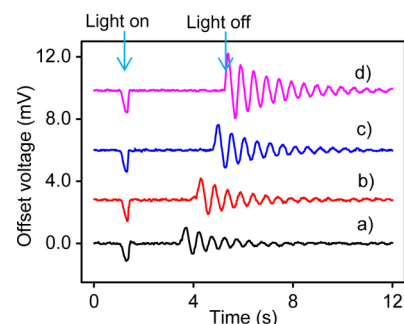

Figure 3. Induction voltage outputs under different time of UV-light exposure of (a) 1, (b) 2, (c) 3, and (d) 4 s. The UV-light intensity is 13.2 mW/cm².

Table 1. Electricity Output of OPG upon UV-Light Exposure with Different Times

exposure time (s)[a]	bending voltage (mV)	max voltage (mV)	period (s)	duration time (s)
1	−1.1	+0.9	0.8	4.0
2	−1.1	+1.4	0.7	5.0
3	−1.1	+1.8	0.6	6.0
4	−1.1	+2.2	0.5	7.0

[a]The representatives of the expose time, bending voltage, max voltage, periodical time, and the duration time are illustrated in Figure S11 in the Suppporting Information.

faster unbending velocity and a longer coil vibration under the magnetic field. In contrast to a free swing bilayer film without a copper coils, the magnitude of the bending angle was found to be dependent on the irradiation time, whereas its bending velocity was seldom changed by light exposure time.[24] In the induction device, the coils were set near the magnetic iron surface for the purpose of the uttermost magnetic flux.
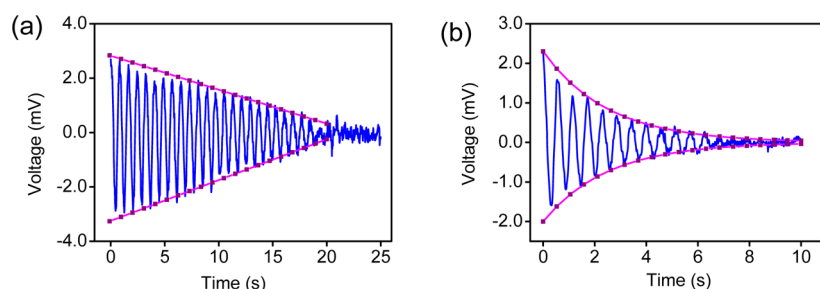
Figure 4. Induction voltages (blue line) show different decreasing tendency after turn the UV-light off, which is depends on the outside load of resistance connected in the circuits. (a), open circuit, the voltages shows an linear decreasing. The voltage amplitude (purple dot line) vs time is fitted by a linear function of $y = m - kx$, where $m = 0.00113$, $k = 5$. (b) With an equivalent resistance $R = 1100$ ohms external resistor connected in the circuits of the coils, the voltage amplitude (purple dot line) vs time is fitted by an exponential function $y = ce^{(-x/t_0)}$, where $c = 0.0023$, $t_0 = 2.5$.
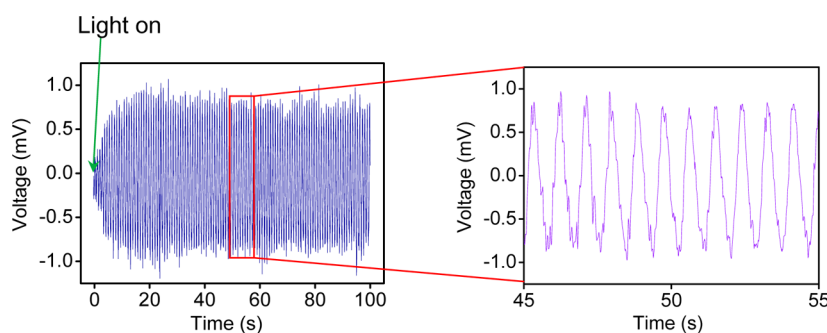

Figure 5. Continuous outputs electricity upon continuous UV-light exposure on an automatically self-shielding bilayer film.

Obviously, the magnetic iron surface blocked the bilayer film bending motion, thus it observed a similar bending voltage (−1.1 mV) under different exposure time. Although the film bending motion was hindered by the magnet, prolonging the exposure time resulted in much more of the trans azobenzene molecules transformed into their cis forms in the photoactive layer, which stored the light energy and increased the modulus of the photoactive layer.[8] Thus, the bilayer film acquired a higher unbending velocity and a fast recovering rate when a longer exposure light was switched off. The calculated electricity conversion efficiency from a UV-light irradiation on one bilayer film (25 mm × 10 mm × 0.04 mm) was about 1.4 × 10^{-3}%. Although it is far lower than the conversion efficiencies of conjugated polymer photovoltaic cells,[25,26] there is a high potential for improvement by optimal the bilayer film and magnetic field. For example, it has a greater possibility of increasing the oscillation rate compared to that of the cantilever reported in White's work (as high as 270 Hz in frequency).[11]

The decrease of the oscillation amplitude in the bending and unbending motions was attributed to the hydrodynamic effects in the White's work.[11] Besides the hydrodynamic effects of the atmosphere, the electrical current passing through the coils presented a crucial role in the damping of the oscillation generator. The decaying of the induction voltage peak of the swinging coils showed two damping effects. When the voltage was measured in the open-circuit mode, the current was opened (Figure 4a), and the decrease in the voltage value showed an envelope of a straight line, suggesting that the slow-down energy was originated from the hydrodynamic effects of the atmosphere. Under the closed current circumstance measurement (Figure 4b), the coils connected to a load resistor with about 1100 ohms. Thus, the current flowing through coils cannot be ignored, and a self-induction current was generated in the coils. According to Lenz's law, such currents will move in

a way that the forces on them oppose the cause producing them. This force on the induced current produced the electromagnetic damping. In this case, the simulation curve (the purple dot line in Figure 4b) fits exactly the behaviors that the outer envelope of the induction voltage peaks is an exponential decay.

To continuously output electricity, we carefully adjusted the light illumination for exposure on the far end of the bilayer film to cause bending motion (Movie S2 in the Supporting Information). When UV-light exposed on the film, the sufficient folding film shielded the light exposure, inducing a fast unbending of the bilayer film. By this way, an alternative exposure and shielding light on the bilayer film generated a continuous oscillation and the swing of the induction coils, thus producing an alternating voltage upon continuous light exposure (Figure 5). The output signals were relatively stable, although the height of the voltage peak for the bending and release appeared differently, which should be caused by the inhomogeneous magnetic flow rather than the fatigue of the bilayer film.

4. CONCLUSION

In summary, we demonstrated a complementary strategy for transferring light energy into electricity using the photodriven pendulum electromagnetic induction generator. The electric-power OPG was fabricated by elegantly combining the photomechanical movement of LCA with the Faraday's law of electromagnetic induction. Electrical measurement of the OPG demonstrated that the output electricity was proportional to the changing rate of the magnetic flux through the coils. The light intensity, film thickness and sample size exhibited strong influence on the movement rate of the coils. Continuously electrical output of OPG was also achieved by self-shielding the light exposure realizing alternatively photoinduced motions of

bending and unbending. The fabricated OPG showed advantages of simplicity, low cost and stability for coupling the photomechanical energy. There are a lot of possibilities of improvement this primary device such as enhancement of photoinduced mechanical force and fast response, optimization the magnetic flux accommodating the swing motion of the induction coils, which is still underway in our lab.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Polymer synthesis and characterization, thermal properties and alignment of the LCE layers, photoresponsive and photomechanical motion of the bilayer film, and opto-mechanical experiments and two movies showing the bending and unbending of OPG upon irradiation of pules and continuous UV light. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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