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Photomechanical Bending of Linear Azobenzene Polymer

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We firstly report a novel strategy for the preparation of rapid and reversible photo-driven actuators consisting of active linear azobenzene polymer layer and passive silk fibroin substrate, avoiding the need for oriented azobenzene liquid crystalline elastomers (LCEs) that have been used until now, just through depositing linear azobenzene polymer onto the top of silk fibroin film. The unimorph actuators can show uniquely different bending properties. Moreover, the response speed of the unimorph actuator is on the level of a few hundreds of millisecond. The bending angle can be well controlled either by changing the UV light intensity or by altering the thickness ratio of the two composed layers. Additionally, complex and attractive arm-like movements are successfully achieved. We believe that the proposed unimorph actuators will pave the way for designing complicated and programmed artificial muscle.

Introduction

Smart soft materials that reversibly change their shape and/or size in response to an environmental stimulus have attracted considerable interest due to their potential applications in diverse fields ranging from robotics, biomedicine to tunable micro-optics.[1-8] The smart materials for fabricating soft actuators include thermal or photo-responsive LCEs[9], electroactive conjugated polymers[10], pH[11] or solvent-responsive gels[12], thermal responsive shape memory polymers[13], and muscle cells[14]. Among others, photo-responsive LCEs, where in the structural change of photoisomerizable chromophores such as azobenzene and cinnamic groups are employed to change the shape and/or size of polymer films by light irradiation[9,15,16], received special attentions because they can directly convert light energy into mechanical energy and light has obvious advantages, such as intrinsically cleanness, high speed, and remote operation. The fabricating of soft actuators based on photo-responsive LCEs, however, much less developed because the actuating mechanisms originally proposed by de Gennes[17] strongly rely on the ability of controlling the orientation of chromophores and mesogens.[18-21] A large contraction can be induced along the director axis during the anisotropic-isotropic transition, providing that the chromophores or mesogens are universally aligned across the whole sample. This photo-mechanical effect was ascribed to the decrease in the order parameter caused by a photochemical reaction such as *trans-cis* isomerization of azobenzene moieties, where in the rod like *trans*-azobenzene moieties stabilize the LC alignment, whereas the bent *cis* forms lower the LC order parameter.[20,21] Three-dimensional deformation such as bending and twisting was achieved by controlling the order of photo-responsive moieties and exploring the absorption gradient of photons in polymer films.[22] The decrease in orientational order occurs only in the surface region facing the incident light, but in the bulk of the film the photo-responsive moieties remain unchanged. As a result, the volume contraction is generated only on the surface layer, thus causing the film to bend toward the irradiation source.[23]

Unimorph is one typical sample of bending actuators in piezoelectric actuators, which are constructed by bonding together one piezoelectric plate and one elastic plate. In such a manner when the actuators are triggered, the piezoelectric transverse strain will be converted to large bending displacement in the perpendicular direction due to the constraining of each component in the actuator structure.[24] The one dimensional beam theory describing the bending displacement is also well established.[25] The merit of the unimorph actuators is that the deflection of bending are only proportional to the transverse strain generated in the active layer, the Yong's modulus and the thickness ratio of the two composed layers. Unimorph structures provided a simple way to magnify volume change of active layer into bending actuation.[2,6,26-29] These successful results inspired us to open up new possibilities to realize light-driven soft actuator based on unimorph structures using linear azobenzene polymer as active layer, since the photoreponsive azobenzene polymers can expand in volume upon UV light irradiation due to photoisomerization between a rod-like *trans* and a bent *cis* isomer in azobenzene moieties.[30-31]

In contrast to the traditional method of achieving the bending actuation based on highly oriented azobenzene LCEs, unimorph actuators possess an different bending character wherein the bending direction do not depend on the alignment of chromophores or mesogens. Therefore, the design of novel unimorph actuator composed of linear azobenzne polymer is particularly important for development of new principles of soft actuators. Herein, we demonstrate that the bilayer approach can be successfully employed to fabricate high-performance light-driven silk fibroin-azobenzene polymer actuators consisting of an active layer of linear azobenzene polymer and a supporting layer of biocompatible silk fibroin film (Scheme 1). Indicating this

novel technology can well amplify the volume change of *trans*-to-*cis* photoisomerization of linear azobenzene polymer.
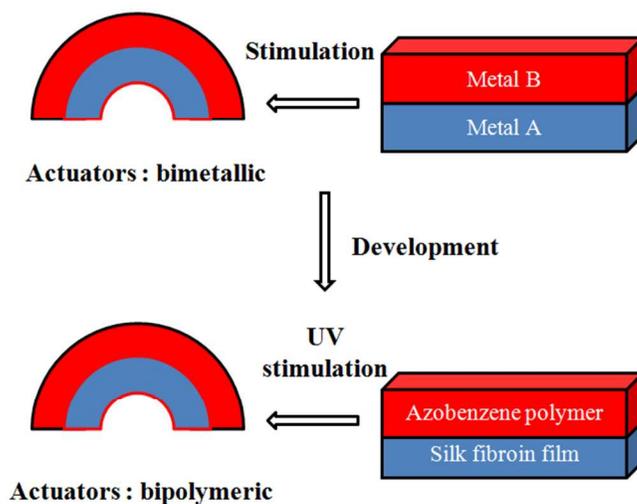
Scheme 1. New strategy for the preparation of silk fibroin-azobenzene polymer actuators (SFA).

Experimental section

Synthesis

Synthesis of 4-(4-methoxy-phenylazo) phenol

Water (15 mL) and 15 mL of 38 wt% HCl solution was added dropwise to the round bottom flask containing 4-methoxyaniline (6.16 g, 0.05 mol). This solution was cooled down to 0-5°C by ice-water bath. Then $NaNO_2$ (8 g, 0.055 mol) in deionized water (20 mL) was added dropwise. The mixture was reacted at 0-5°C for 30 min. Then, NaOH (5.0 g, 0.125 mol) and phenol (7.0 g, 0.075 mol) was added, the solution was kept at 0°C for 4 hour. The resulting yellow crystal was filtered out and dried under vacuum. The precipitate was used without any further purification in the next reaction step.

Synthesis of 1-(4-(hex-5-enyloxy)phenyl)-2-phenyldiazene

4-(4-methoxy-phenylazo) phenol (2.12 g, 0.0093 mol) was dissolved in 50 ml of DMF, NaH (780 mg) were added. The mixture was heated to 80 °C with stirring, and 6-bromo-1-hexen (5.5 g, 0.0 095 mol) was added dropwise to the reaction mixture. The mixture was reacted 24 h at 80°C. Then, the reaction mixture was cooled to room temperature and poured into deionized water (1 L). The precipitated was collected by filtration and purified by silica gel chromatography with a petroleum ether/ethyl acetate (5: 1, v/v) mixture as eluent to yield the final product.[32] (^{1}H NMR (CDCl$_3$, Figure S1): 7.86-8.13 (m, 4H, aromatic), 6.84-7.21 (m, 4H, aromatic), 5.78-6.02 (m, 1H, C*H*=), 4.82-5.25 (m, 2H, C*H$_2$*=), 4.04-4.18 (t, 2H, ArOC*H$_2$*-), 3.87(s, 1H, CH$_3$O-); Elemental analysis: calculated (%): C 73.52, H 7.14, N 9.03; Found (%): C 73. 21, H 6.98, N 9.04.

Synthesis of azobenzene polymer, PsAzo

A 50 mL flask was filled with poly[oxy(methylsilylene)] (PHMS) (0.5 g, 0.0077 mol Si-H), 1-(4-(hex-5-enyloxy)phenyl)-2-phenyldiazene (1.84 g (100 mol% of the Si-H), and toluene (30 mL), and 0.0029 mg (mole ratio, Pt : alkene group = 1 : 10^3) of

the chloroplatinic acid catalyst (H$_2$PtCl$_6$) were added. The solution was kept in absolute dry and oxygen-free, nitrogen atmosphere, and heated at 110 °C for 24 h. Then the solution was cooled down to room temperature and precipitated in petroleum ether three times, and dried. The yield of polymer is 2.07 g (85%).[33] The molecular weight (M_n = 24700 g/mol) and polydispersity index (PDI = 2.1) of PsAzo were obtained by GPC. (^{1}H NMR (CDCl$_3$, Figure S3): 7.72-8.21 (m, 4H, aromatic), 6.58-7.20 (m, 4H, aromatic), 4.78-4.92 (s, 1H, Si-*H*), 3.68-4.26 (t, 2H, ArOC*H$_2$*-), 3.23-3.67(s, 1H, C*H$_3$*O-). The 13 : 1 ratio of the corresponding integration values for the c and k peaks in Figure S3 suggested that molar content of PsAZO chain was about 76%.

Characterization

^{1}H nuclear magnetic resonance (NMR) spectra of synthesized materials were recorded by using a UNITY INOVA 400 (400. MHz for 1H) spectrometer with deuterated chloroform (CDCl$_3$) as the solvent, TMS as the internal standard. Chemical shifts were expressed in parts per million (ppm). The weight-average molecular weight and polydispersity index of azobenzene polymer PsAzo were evaluated using gel permeation chromatography (GPC) (GPC; waters1515, column; PLgel 10 μm MIXED-B) using THF as eluent at a rate of 1 mL/min at 30 °C and poly(methyl methacrylate) (PMMA) as standards. The images and movies of the SFA actuators were taken with a digital camera (Sony HDR-XR550). The mechanical force generated in the film and tensile strength σ or Yong's modulus E was measured by Dynamic Mechanical Analyzer (DMA, DMA-Q800, American TA instrument). The cross-sectional image of the film was obtained by optical microscope (Leica DM4000). Ultraviolet visible (UV-vis) absorption spectra of film were analyzed by UV-3600. The thermodynamic properties of the monomer and polymer were analyzed by a differential scanning calorimeter (DSC; DSC-2010, American TA Instrument) at a rate of

10°C/min in both heating and cooling cycles. The liquid crystalline (LC) phases were determined by polarizing optical microscope (POM).
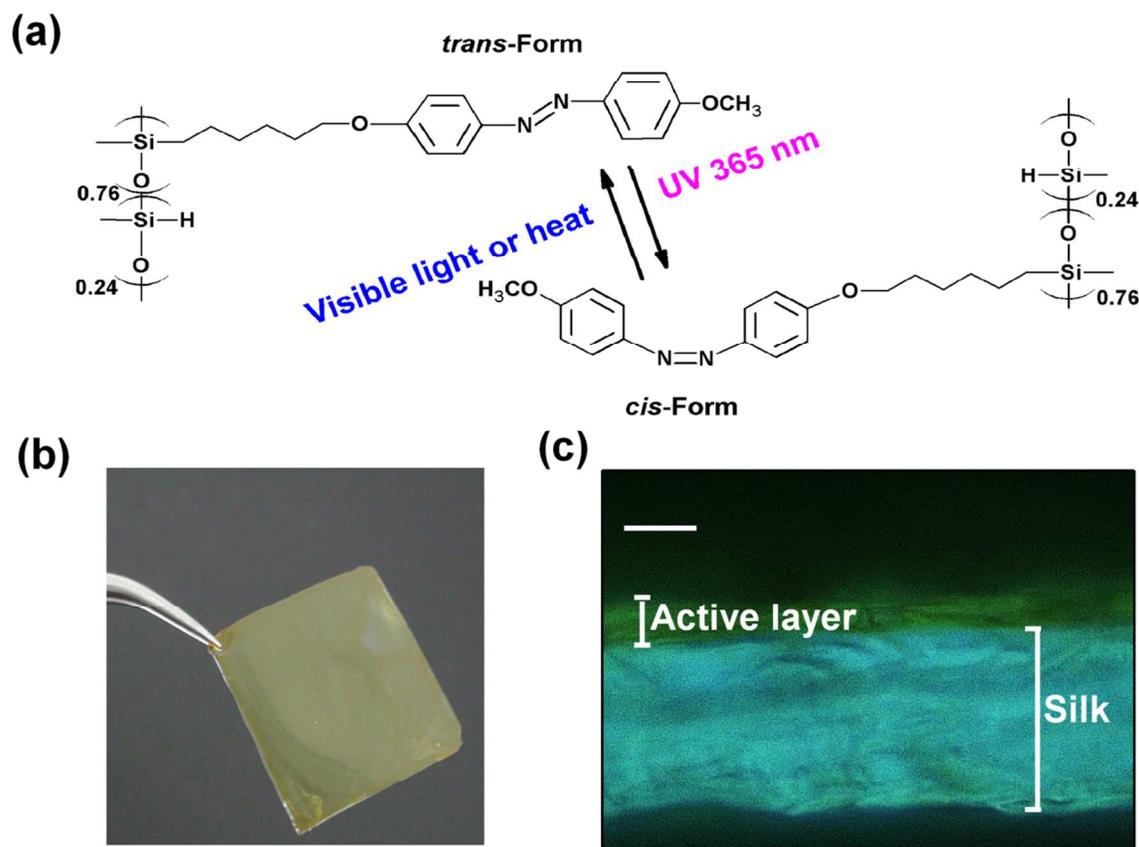
Figure 1. (a) Chemical structure of azobenzene polymer PsAzo and the structure changes of azobenzene group in response to UV light and visible light or heat. (b) The macroscopic view of SFA actuators. (c) Cross-sectional optical microscope image of SFA actuators.

Results and discussion

The chemical structure of the photo-responsive azobenzene polymer (PsAzo) and its structural transformation upon alternate irradiation with UV and visible light or heat, are shown in Figure 1a. The synthesis and characterization of PsAzo are given in FigureS1-S4, which shows a relatively low glass transition temperature (T_g) (about 19°C at a heating rate of 10°C/min), and rapid photoisomerization between a rod-like *trans* and a bent *cis* isomer upon UV light irradiation (Figure S5). Silk fibroin film is chosen as elastic plate because of its optical transparency (>90% transmission in the visible spectrum)[34], outstanding mechanical robustness and biocompatibility[35-38]. The PsAzo has an ultimate tensile strength σ of 1.3 Mpa and Yong's modulus E of 52.3 Mpa, while the σ and E values of the silk fibroin film prepared in the current study are 12.5 Mpa and 753.1Mpa. Eventually, the merit of both of them make the bilayer system mechanical robust and flexible (Figure 1b). The silk fibroin-azobenzene polymer (SFA) actuators were prepared simply by spin casting the linear azobenzene polymer PsAzo onto free standing silk fibroin films. Figure 1c show typical examples cross-sectional view images of the SFA films with active layer (~ 2 μm in thickness) and the passive substrate silk fibroin (~ 12 μm in thickness).

Upon UV light irradiation, photoisomerization between a rod-like *trans* and a bent *cis* isomer can take place in the azobenzene moieties of the active polymer. The photoreaction due to UV light irradiation would decrease the density of the azobenzene polymers and cause the expansion in volume[30]. By contrast, the silk fibroin layer is inert to light. The obvious difference in response to UV light, combined with their high flexibility and mechanical robustness can produce mismatched strain in the two different layers and induce bending upon UV light irradiation. As a proof of concept, a cantilever (2 mm × 12 mm × 16 μm) is cut from the initial large-area uniform films. When the active polymer side is irradiated with UV light (365 nm, 70 mW/cm²), the cantilever, immediately bends away from the light source. Once the UV light is switched off, the cantilever quickly returns to its straight position while the shape remains unchanged, as shown in Figure 2 and Movie S1. What's worthy paying attention to is that it bends immediately toward the UV light source, when the cantilever is irradiated from the silk fibroin side (Figure 2). In addition, if single silk fibroin film is irradiated with UV light, however, no bending behavior is observed. Indicating the distinguishing characteristics of SFA actuators is that the bending

direction does not depend on the direction of the UV light, because volume expansion of the active polymer indeed takes

place, and the volume of the silk fibroin substrate keeps constant upon UV light irradiation.
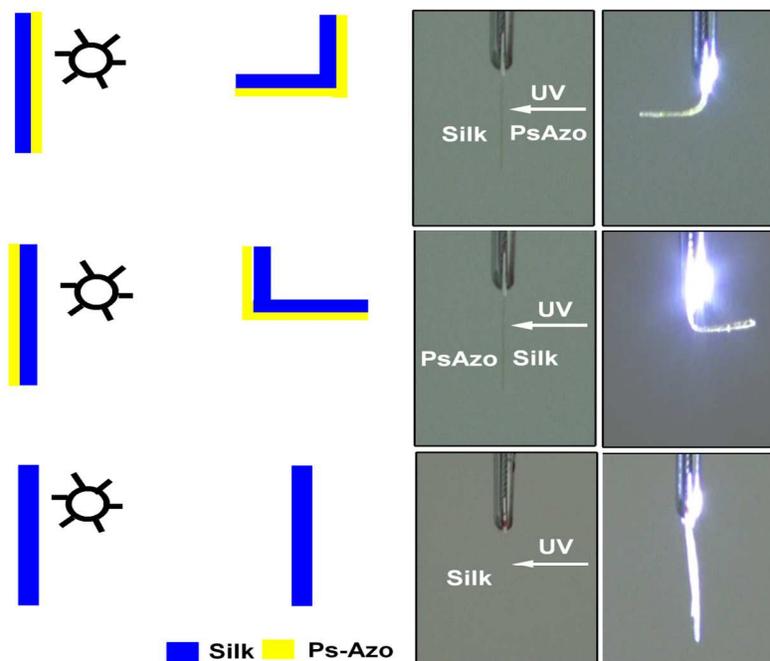
Figure 2. (a) Schematic representation of the muscle-like motion in the presence of UV light on or off (365 nm, 70 mW/cm^2) and the corresponding actual pictures of the process (the size of the SFA actuators: 2 mm × 12 mm × 16 um).

The excellent SFA unimorph actuator shows very high response speed. As shown in Figure 3, the bending angle can be as large as 115° within 0.9 seconds upon UV light irradiation (365 nm, 70 mW/cm^2). It has to be mentioned that the bending is rapid and the final equilibrium shape (at 90°) is reached within 4 seconds. Once the UV light is turned off, the cantilever quickly recovers to its initial state within 3 seconds. The corresponding pictures of the motion are shown in Figure S6. In addition, the bending behaviors can be repeated for many times. Figure 3b depicts the reversibility of the bending angle on UV light irradiation (365 nm, 70 mW/cm^2) without any fatigue over time (Movie S2). Those above results indicated that SFA actuator gives hope to develop a novel soft photomechanical actuator.

According to the beam theory describing the bending displacement of unimorph actuators, the driving force of the SFA actuators is the transverse strain generated in the active layer, which is proportional to the expansion coefficient of the active layer and the intensity of external stimulus. The bending angle of the SFA actuator is investigated by precisely controlling the UV light intensity. As shown in Figure 4a, the bending angle exponentially rises with the increasing of UV light intensity. This indicates, on the one hand, the expansion coefficient of the azobenzene polymer is not linear in the measured intensity range; on the other hand, the bending actuation of the SFA actuator can be well controlled by the input intensity of stimulus. The bending angle also depends on the thickness ratio of the two composed layers. The SFA actuator with different thickness of silk fibroin film while keeping the thickness of the active layer constant (2 μm) are examined. As shown in Figure 4b, the bending angle can

reach 90° when the thickness of the silk fibroin film is smaller than 17 μm. With further increasing film thickness of silk fibroin,
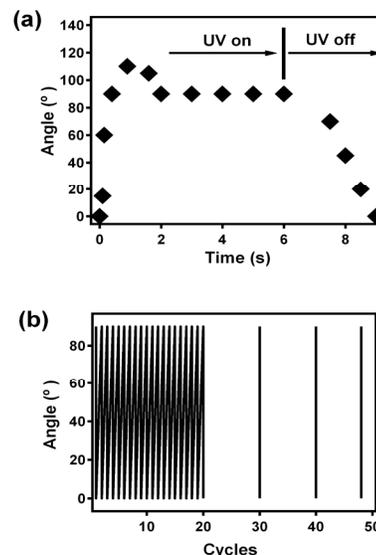
Figure 3. (a) Bending angles of the SFA actuators as a function of the irradiation time when UV is on and off (365 nm, 70 mW/cm^2). (b) The bending cycles of SFA actuators between 90° and 0°.

the bending angles are nearly exponentially reduced. It should be pointed out that the standard deviation (SD) was ± 5° in Figure 3 and Figure 4. These phenomena reveal that the bending angle of the novel SFA actuator can be well controlled either by tuning the

UV light intensity or by precisely altering the thickness ratio of the two composed layers.
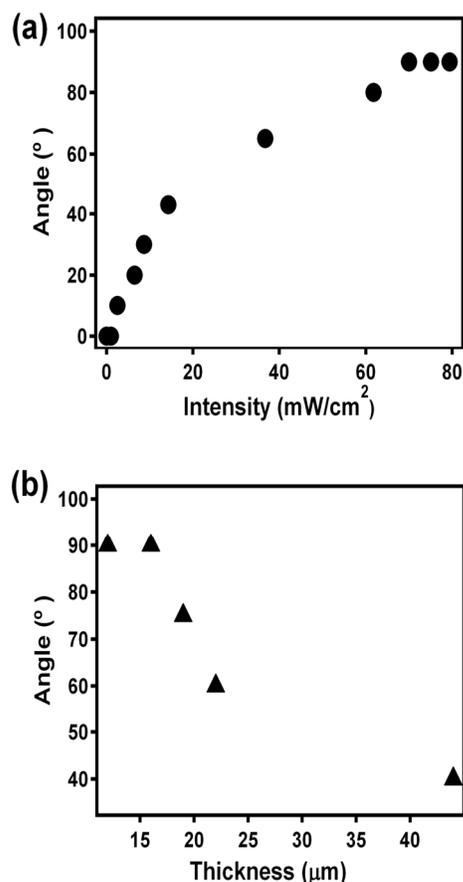
Figure 4. (a) The dependence of bending angle on the light intensity. (b) The dependence of bending angle on the thickness of silk fibroin film (PsAzo: 2 μm, UV light intensity: 70 mW/cm^2).

The stress generated from photo-driven SFA actuators is measured by a thermo-mechanical analysis. As shown in Figure 3a, the cantilever is fixed by clamping both ends of the film at room temperature and tested in tension in a strain-controlled dynamic mechanical analyzer held with a 5×10^{-4} % strain and 40 mN preload to pretention the film. Upon irradiation of the UV light, the generated stress of the films sharply increases to at least 5 MPa in one minute. A little decay is shown when it increases to the summit with the irradiation time of the UV light going up. The stress slowly returns to 0 when the light is turned off (Figure 5). The increase in stress is very pronounced, which indicated that the deformation in SFA actuators is elastic rather than plastic.
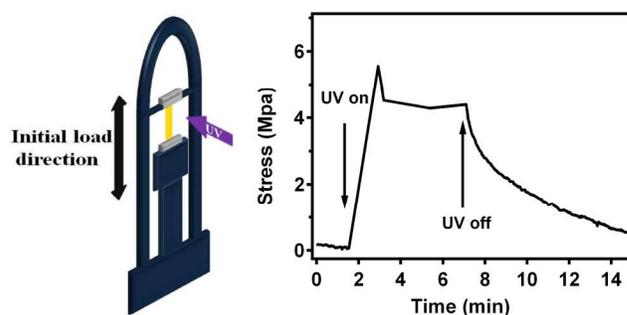
Figure 5. Schematic illustration of the experimental setup and the stress generated from the SFA actuators upon irradiation with UV light (365 nm, 70 mW/cm^2) (2 mm × 12 mm × 16 um) and recovery process.

Because the excellent SFA unimorph actuators can be easily prepared by the spin cast method, complex architecture is designed to mimic the movement of arms. Three separated regions on the surface of silk fibroin film are coated with PsAzo and can behave as the joints in arms upon sequencing UV light irradiation, as shown in Figure 6a. A rectangle film (25 mm × 3.5 mm × 16 μm) is carried out to achieve the programmed movement. Initially, the pot marked with 1 is mainly irradiated with UV light leading to the bending of the first place. Next, UV light mostly turns to 2 to trigger the second bending behavior, while the first irradiated pot keeps balanced. In the end, the UV light is moved to 3 to induce the bending to complete complex simulating robotics arm's movement. Moreover, self-recovery process is also finished just by turning the UV light off. Figure 6b captures the real optical images of programmed bending-unbending behaviors. Noted, the entire bending process just takes 7 s, and self-recovery process can be completed gradually in only 10 s (Movie S3). Particular, the whole process is controlled just by the UV light irradiated location and direction that could realize remote control and automatic recovery.
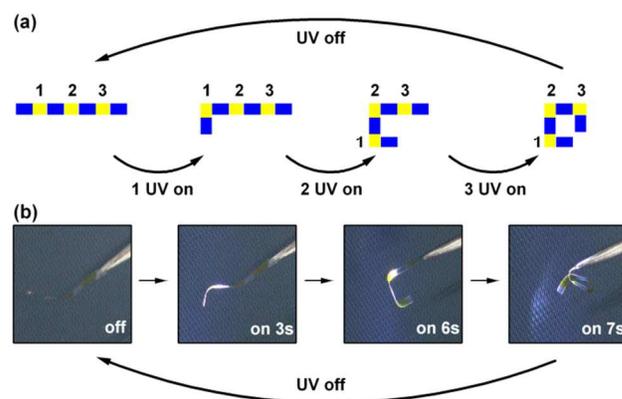
Figure 6. (a) Fabrication scheme for robot arm based on SFA actuators. (b) The bending behavior of robot arm by photo-induced actuation (365 nm, 70 mW/cm^2) and self-recovery behavior by tuning off the UV.

Conclusions

In summary, the novel unimorph structure consisting of an active layer of linear azobenzene polymer and a supporting layer of silk fibroin film was successfully used to fabricate highly tunable, photo-driven soft actuators. In contrast to the conventional LCEs approaches for fabricating photo-driven actuators by controlling the orientational order of chromophores and mesogens, the volume change during *trans*-to-*cis* photoisomerization of linear azobenzene polymer are amplified by the unimorph structures. In addition, the photo-switching muscle-like movement was fast and reproducible without obvious fatigue. Therefore, we believe that this novel SFA actuator will open a new way for designing intelligence devices for biological and medicine.

Acknowledgments

Notes and references

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† Electronic Supplementary Information (ESI) available: [supplementary data, including (1) Materials; (2) characterization of azobenzene materials (Figure S1-S4); (3) the preparation of the silk fibroin solution; (4) the preparation of silk fibroin-azobenzene polymer (SFA) actuators; (5) the UV spectra of PsAzo film (Figure S5); (6) The process of reversible bending of SFA actuators alternate controlled with UV (Figure S6).]. See DOI: 10.1039/b000000x/

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