Chapter 10
Nanotechnology and Nanomaterials in Photodeformable Liquid Crystalline Polymers

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Abstract The combination of nanomaterials and ordered deformable soft materials is emerging as an enabling system in nanoscience and nanotechnology. In this context, nanomaterial functionalized photoresponsive liquid crystalline polymers are very promising and versatile systems due to their dynamic function. Moreover, the unique characteristic of nanomaterials combined with the mechanical, self-organizing and stimuli-responsive properties of deformable liquid crystalline polymers opens up new and exciting possibilities. In this chapter, we present recent developments of photodeformable behaviors of liquid crystalline polymers functionalized with nanomaterials. The main emphasis revolves around how the physicochemical properties of different nanomaterials modulate the reversible photomechanical behaviors of liquid crystalline polymers and their potential application in devices such as optically controlled switches and soft actuators.

10.1 Introduction

Stimuli-responsive materials have sparked enormous interest in recent years due to their potential applications in micro-machines, soft robots, biomedical systems, etc. [1–6]. A variety of intelligent polymeric materials such as shape memory polymers [7, 8], polymer gels [9, 10], conducting polymers [11, 12], and dielectric elastomers [13, 14] have been developed for these applications. Compared to other stimulus-driven methods including pressure [15], heat [16, 17], electric field

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[18, 19], magnetic field [20], and pH [21], light is particularly attractive because it can provide remote, instant and precise noncontact control. Thus, photoresponsive polymers that can deform in response to light have become a hot topic in both academic and industrial fields. Among all the photoresponsive polymers, liquid crystalline polymers (LCPs) with anisotropic mesogens in the side or main chains have been attracting more and more attentions because of their advantages: (1) They elegantly combine self-organization properties of liquid crystals (LCs) with the mechanical properties of polymers; (2) They show reversible photode-formable behaviours because of the photoisomerization of photo crosslinking moieties such as azobenzene and cinnamate groups; (3) They exhibit large shape deformations with relatively weak forces due to the amplification of the response by the cooperative motion of mesogenic moieties; and (4) Their preferential deformations can be precisely controlled by the orientation of mesogenic moieties.

In recent years, nanotechnology and nanomaterials have been widely used in designing advanced functional materials based on photoresponsive LCPs. Although several reviews have concentrated on the photodeformable effect of LCPs and their applications in soft actuators [22], to date the influence of nano-structures and nanomaterials on the photodeformable properties of LCPs has not been summarized. In this chapter, we mainly focus on the utilization of special nanostructures and amazing physicochemical properties of nanomaterials to manipulate the photomechanical behaviors of LCPs. Furthermore, their potential applications as light-driven devices and other future prospects are proposed.

10.2 Mechanism of Photoinduced Deformation in LCPs

Generally, azobenzene is one of the most extensively studied photochromic groups due to its unique properties such as photoisomerization, photoinduced phase transition and photo-triggered cooperative motion in LC systems [23–31]. Espe-cially, the LCPs with azobenzene acting as both a mesogen and a photoresponsive chromophore in the side chain dominate the research field of photo-driven LCPs. In this system, "bimetal model" is reasonable to explain the photomechanical behaviors of LCPs [32]. As shown in the left of Fig. 10.1, when mesogens are oriented parallel to the surface of LCP films, defined as the homogeneous align-ment, volume contraction is often generated along this pre-aligned direction leading to the anisotropic bending behavior towards a light source. According to the "bimetal model", *trans*-to-*cis* photoisomerization takes place only in the surface area of LCPs since the molar extinction coefficient (ε) of azobenzene moieties at around 360 nm is very large (on the order of 10^4 L/mol cm), causing incident photons to be absorbed just in the surface of LCP films (a thickness of several tens of microns). Thus, these LCP films can be considered as a bilayer structure in which the upper layer is active layer and the bottom layer is passive one. As a result, the volume contraction is produced only in the surface layer from the irradiated side, which causes LCPs to bend toward the light source. On the

Fig. 10.1 Plausible mechanism of different photoinduced deformation behaviors of LCPs with their mesogens in homogeneous and homeotropic alignment states, respectively. Reproduced with permission from [33]. Copyright 2013
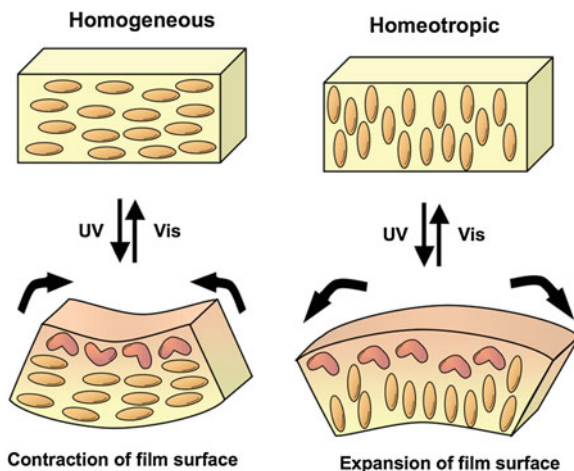

contrary, when mesogens are oriented perpendicular to the surface of LCPs, a different photodeformable behavior of bending away from the light source occurs due to the volume expansion of the upper layer (active layer) of LCP films [33]. Additionally, the photodeformable behavior of LCPs is reversible because of the reversible photoinduced phase transition and the change of mesogenic orientation.

10.3 Application of Nanotechnology and Nanomaterials in Photo-Driven Actuators of LCPs

Because of the unique photodeformable behavior of LCPs, a variety of soft actuators such as flexible inchworm walkers [34], plastic motors [35] and high-frequency oscillators [36] have been designed. For these soft photo-driven actuators based on LCPs, many factors determine the photo-driven behaviors of actuators, including the wavelength, polarization direction and intensity of the light source, and inherent parameters of actuators such as the concentration of azobenzene moieties, the crosslinking density and the molecular arrangement within actuators. Besides, their mechanical properties, conductivity and overall physical attributes should also be taken into consideration for practical applications (see in Fig. 10.2).

In order to meet these requirements for the application of LCPs in different areas, the research concerning nanotechnology and nanomaterials in photo-driven actuators made from LCPs has been focused on the following aspects: (1) Design of special nanostructures as the nanotemplate for the molecular arrangement of mesogens; (2) Utilization of nanomaterials as a photo-absorbing agent and thermal source to trigger the phase transition of azobenzene due to their photothermal
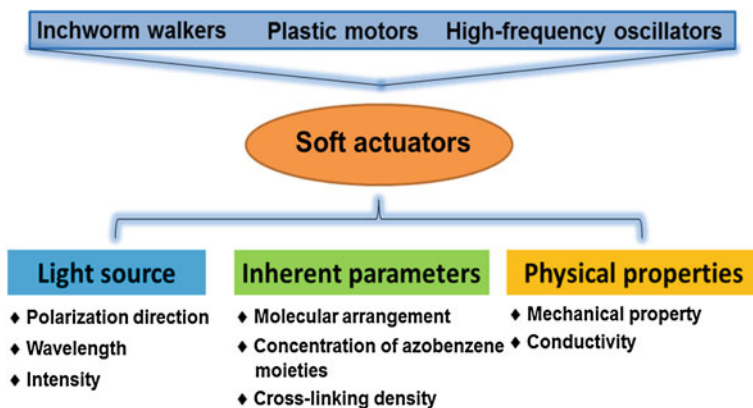
Fig. 10.2 Influencing factors for potential applications of soft actuators based on LCPs

effect; and (3) Using upconversion nanomaterials to adjust the wavelength of the light inducing the deformation of LCPs. Herein, the influence of nanostructures and nanomaterials on the photomechanical effect of LCPs will be discussed in detail based on these three aspects.

### 10.3.1 Template for Alignment of Mesogens

As mentioned in Sect. 10.2, the alignment of mesogens and the pre-treatment condition play a dominated role in the photodeformable behaviors of LCPs. Mechanically-treated methods utilizing stretching or rubbing have been typically applied to align mesogenic molecules. For instance, Finkelmann and coworkers first fabricated crosslinked LCP (CLCP) film with reversible photoinduced deformation by a two-step method [37]. In this method, well-defined networks were synthesized in the first step and then mesogens were well aligned along with the stretching direction and cross-linked to fix the ordered mesogens in the second step. Although a large contraction ratio of 20 % was achieved, harsh conditions such as the fast reaction rate of vinyl groups and fixation of ordered mesogens with a constant load were required. It is well known that mechanical rubbing of a polymer film (polyvinyl alcohol or polyimide) on a substrate has been widely adopted for the production of LC display devices. Undoubtedly, broken debris and structural damage often occur because of the dust and electrostatic charge generated in the fabrication process. To overcome these existing issues of mechanical method for aligning LCs, a self-assembled nanoporous structure has been fabricated as a nanotemplate for LC alignment [38]. As shown in Fig. 10.3a, the nanoporous structures can be generated by the extrusion and uniaxial stretching of the polymer film, and polyethylene (PE), polypropylene (PP) and polyamide (PA)
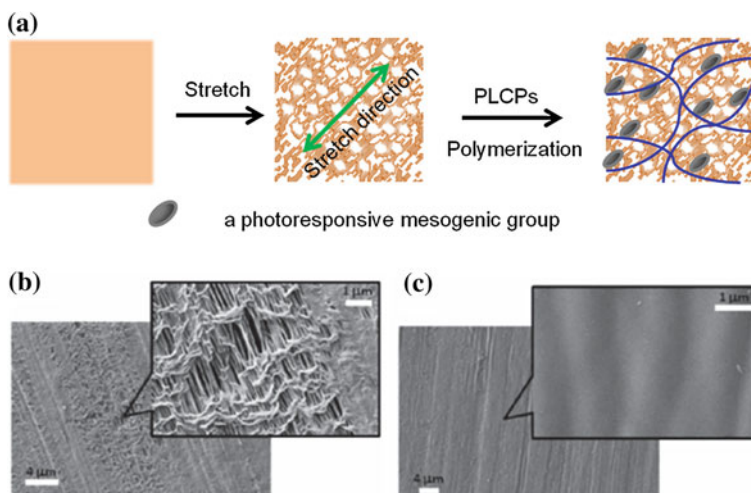
Fig. 10.3 Scheme of the preparation of nanoporous polymer template by stretch method and LCP composite film with mesogens highly aligning along with the stretch direction (**a**). SEM images of the initial porous polymer film (**b**) and the polymer composite film after filling with LC mixture and polymerization (**c**). Reproduced with permission from [38]. Copyright 2013

with a high crystallinity (~ 50 %) all can be used as such a polymer. Figure 10.3b shows a typical nanoporous structure of the polymer film, which just looks like composed of many parallel grooves. After immersing the nanoporous polymer film into the molten LC mixture and allowing thermal polymerization, the nanopores were filled with the CLCPs (see Fig. 10.3c). Upon irradiation with UV light, a strong bending behavior parallel to the stretching direction was observed in the nanocomposite film and it recovered to its initial state after the removal of the light source. Thus, the reversible photomechanical behavior can be attributed to the mesogens well aligned along the stretching direction induced by the self-assembled nanoporous structure. Moreover, the nanoporous polymer film functions as not only a template to orient mesogens but also an ideal matrix to provide excellent mechanical properties for these actuators. Although the excellent alignment behavior of LCs can be induced by these self-assembled nanoporous structures, the preparation process of the nanoporous structure is complicated and nanopore size distribution is not uniform. Additionally, the mechanism of LC alignment induced by the nanoporous structure is still unclear. Moreover, the morphology and size of nanopores are assumed to play an important role in inducing the LC alignment. Thus, the development of a convenient method to prepare nanoporous structures with uniform and controlled pore sizes is a promising way to align LCs and to explore the mechanism of LC alignment induced by the nanoporous structure.

For practical applications, the photoinduced deformation of LCPs should be accurately controlled in a designed way. As the photomechanical behavior of LCPs is closely related to the alignment direction of mesogens, multiple
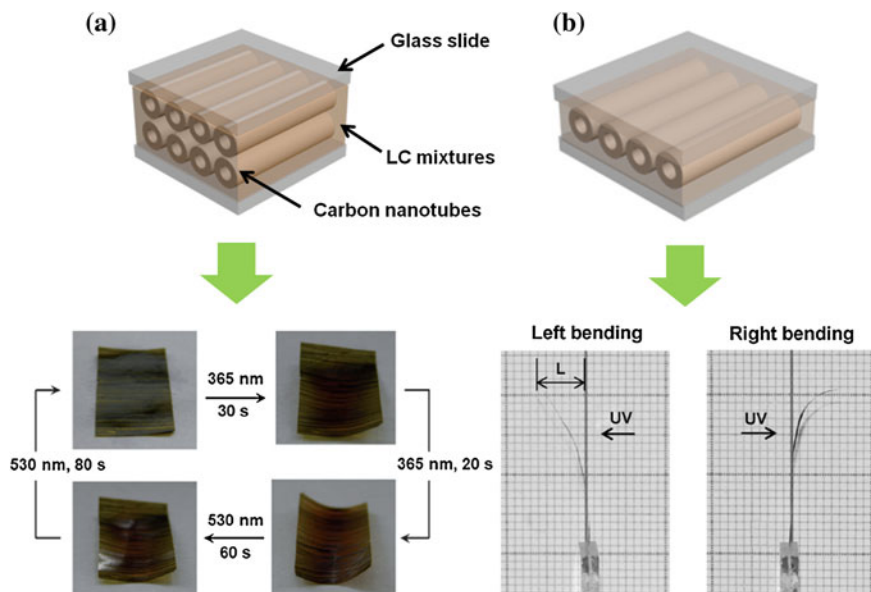
Fig. 10.4 Scheme of the preparation process of **a** CLCP nanocomposite film with mesogens oriented parallel to CNTs and **b** CLCP nanocomposite film with mesogens oriented perpendicularly to CNTs and their distinctive photomechanical behaviors. Reproduced with permission from [39, 40]. Copyright 2013

orientation directions are most desired, which can be induced by the self-assembled nanostructures. Recently, the CLCP, fabricated by utilization of ordered carbon nanotubes (CNTs) as a template to induce the LC alignment nanocomposites, were reported to exhibit excellent photodeformable behavior [39, 40]. In Fig. 10.4a, the CLCP nanocomposites showed distinctive photodeformable behaviors when they were fabricated with different preparation processes. Molten mixtures of the liquid crystalline monomer, initiator and crosslinker were injected into a LC cell that was made of two CNTs-sheet-covered glass slides with CNTs sheet inside. The freestanding CLCP nanocomposite film was obtained by photopolymerization at the liquid crystalline phase. A rapid and reversible photoinduced deformation was achieved by alternating UV and visible light irradiation, and the CLCP nanocomposite film curled along the aligned direction of CNTs indicating mesogens oriented parallel to the align direction of CNTs. This phenomenon might result from the structure of CNTs' sheet performing the same function as the surface of a rubbed polyimide film.

In Fig. 10.4b, the CLCP nanocomposite film was fabricated via a different process. The LC monomer, initiator and crosslinker were all dissolved in the solvent and doped onto the CNT strip. The CLCP nanocomposite film was achieved by the photopolymerization of CNT strip in the LC cell without CNT sheets. Interestingly, a unique photomechanical behavior of the CLCP

nanocomposite film bending away from the light source was observed, indicating that mesogens would be oriented perpendicular to the alignment direction of CNTs. It was assumed that the mechanism of alignment of mesogens induced by CNTs was related to many facets such as the special nanostructures of CNTs, non-covalent interactions between the CNTs and mesogens, and the preparation method of the CLCP nanocomposite. These will be further elucidated through continued experiments and efforts in the future. Overall, the mechanical properties and conductivity of CLCP nanocomposites can be greatly improved by the incorporation of CNTs.

10.3.2 Nanomaterials for Wavelength Regulation

It is well known that the wavelength and intensity of the light source triggering the photodeformable behaviors of LCPs are greatly determined by their application areas. For example, near infrared (NIR) light is a more attractive source of optical stimulus in biological systems compared to UV or visible light because the relatively long wavelength light scatters less and penetrates deeper into tissues and also causes less damage to organisms. As a result, the control of the wavelength of the activating light source by nanomaterials has been a hot topic in recent years. Based on the mechanism that the material responds to light, two strategies to manipulate this wavelength have been developed. One is to utilize the photo-thermal effect of nanomaterials and the other is to use the frequency shifting of upconversion nanomaterials.

10.3.2.1 Photothermal Effect

The photothermal effect of nanomaterials such as CNTs, graphenes, graphene oxides, and gold nanoparticles has been used in biomedical domain for hyper-thermia therapy [41]. The photothermal effect of nanomaterials is shown in Fig. 10.5, in which nanomaterials strongly absorb the light with a characteristic frequency and transfer the light energy into heat due to internal conversion or the losses in the surface plasmon resonance (SPR). Because the photodeformable behavior of LCPs is attributed to the phase transition from an LC to isotropic state, which can be induced by the light or heat, the photothermal effect of nanomaterials can be considered as a promising method for controlling the responsive wavelength for the photoinduced deformation.

Several groups have selected CNTs as the photo-absorbing agent to induce the photodeformable behavior of LCPs because of their strong absorption in the visible and NIR region [42–45]. However, sensitivity and stability are relatively low in the case of an indirect photo-actuation of CNTs randomly dispersed in LCPs. To achieve excellent photodeformable behavior, both excellent dispersion property and alignment of CNTs in LCPs are required. Chen and coworkers fabricated
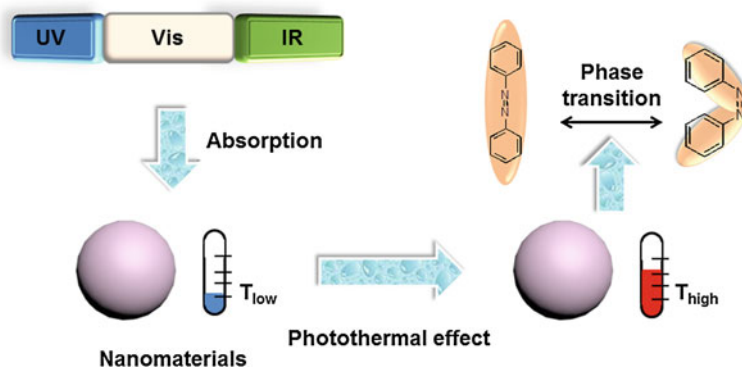
Fig. 10.5 Schematic illustrations of the photothermal effect of nanomaterials and the mechanism of the photomechanical behavior induced by the photothermal effect of nanomaterials

photo-driven deformable bilayer nanocomposite films based on the CNTs/LC elastomers and silicone, in which the CNT/LC elastomer acted as an active layer with silicone as the passive layer [46]. A large and stable deformation can be reversibly triggered by IR light due to the mechanical stretching induced by the photothermal effect of CNTs and their self-assembling behavior in the LCPs. The inchworm walker and artificial arm were realized by delicate structural design based on these bilayer nanocomposite films.

Similar to CNTs, gold-based nanomaterials have been explored for their excellent photothermal properties and are widely applied in the biomedical field due to their stability, biocompatibility and wavelength tunable SPR position. The SPR of gold nanoparticles is closely related to their shape, size and structure, which means that the characteristic wavelength of the SPR can be accurately prescribed by controlling the synthesis of gold nanoparticles [47–52]. Although few studies concerning the use of the photothermal effect of gold nanoparticles to induce photomechanical behavior of LCPs have been reported, gold nanoparticles are more convenient and suitable for regulating the wavelength sensitivity of nanocomposites when compared to CNTs.

10.3.2.2 Upconversion Nanomaterials

Upconversion nanomaterials are "frequency modulation" particles that can absorb multiple photons with the wavelength of λ_1 and then emit corresponding photons with the principal wavelength of λ_2 (Fig. 10.6), where the emission wavelength is shorter than the excitation wavelength. If the emission wavelength of upconversion nanomaterials λ_2 can match with that of the light inducing the *trans*-to-*cis* isomerization of azobenzene chromophores, the reversible photomechanical behavior of LCPs can be accomplished by light with a wavelength of λ_1. The above-mentioned process shows how upconversion nanomaterials can be used to regulate
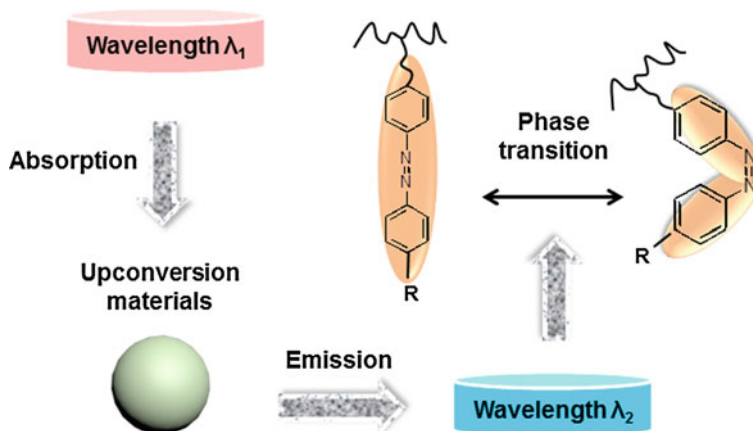
Fig. 10.6 Schematic illustration of the frequency modulating function of upconversion nanomaterials and the mechanism of the photomechanical behavior induced by upconversion nanomaterials

the wavelength of the stimulating light source. However, the emission wavelength of upconversion nanomaterials λ_2 is typically located in the visible spectrum and the wavelength of light triggering the *trans*-to-*cis* isomerization of azobenzene chromophores is located in the UV region. This mismatching of wavelengths presents a challenge for this strategy.

In order to overcome this issue, a solution is to adjust the wavelength of the light inducing the *trans*-to-*cis* isomerization to visible region by designing molecular structures containing azobenzene chromophores and to fabricate corresponding upconversion nanomaterials that have the appropriate wavelength, simultaneously. For example, a longer conjugated azotolane structure grafted to the side chain of LCPs followed by mixing the upcoversion nanoparticles. The resultant LCP films underwent photoinduced bending and unbending deformation by manipulating the actinic visible light [53]. For the purpose of matching the wavelength of the light inducing the *trans*-to-*cis* isomerization, corresponding upconversion nanoparticles of NaYF$_4$ were subsequently prepared [54]. As shown in Fig. 10.7, the main emission wavelengths of the upconversion nanomaterials were 450 and 475 nm that were in accordance with the wavelength of *trans*-to-*cis* photoisomerization of the azotolane moieties. Therefore, the photoinduced bending behavior of these LCPs can be triggered by NIR light with a wavelength of 980 nm. However, a relatively high excitation power density of 15 W/cm^2 of NIR light was required and the associated heating effect could restrain the potential applications of this scheme. Thus, a red-to-blue triplet-triplet annihilation (TTA) based upconversion system with a high absolute quantum yield of 9.3 $\pm$ 0.5 % was prepared. The generated composite film bent towards the light source when it was irradiated with 635-nm laser at relatively low power density of 200 mW/cm^2 [55].
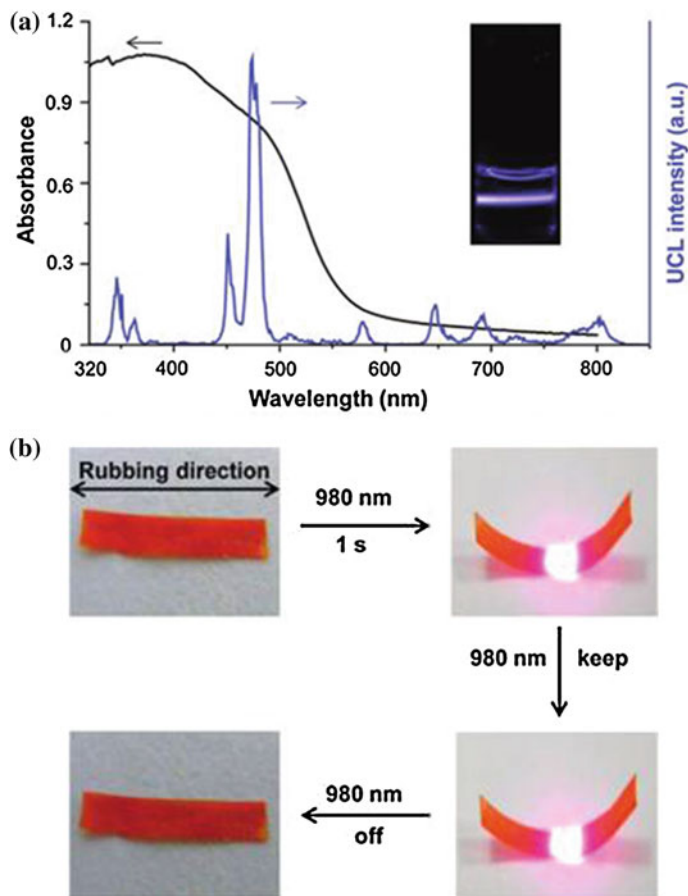
Fig. 10.7 a UCL emission spectrum (*blue line*) of a colloidal CHCl$_3$ solution of UCNPs excited with a 980 nm CW laser and the UV–vis absorption spectrum (*black line*) of the azotalane CLCP film. **b** Photographs of the azotolane CLCP/UCNP composite film bending toward the light source along the alignment direction of the mesogens, remaining bent in response to the CW NIR irradiation at 980 nm, and becoming flat again after the light source was removed. Reproduced with permission from [49]. Copyright 2013

10.4 Soft Actuators Based on Nanomaterials Functionalized LCPs

As mentioned in Sect. 10.3.2, nanomaterials can be utilized to allow design flexibility of the wavelength of the stimulating light source triggering the photo-mechanical behavior of LCPs. At the same time, the functionalization of LCPs has been achieved by the incorporation of nanomaterials, which greatly extends their applications in many fields. Compared to another important class of smart moving
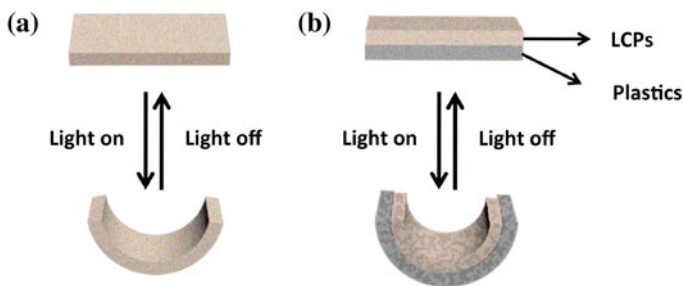
Fig. 10.8 a Reversible photomechanical behavior of LCPs. **b** Reversible photomechanical behavior of bilayer structure composed of LCPs acting as an active layer and plastics without photoresponsive behavior as a passive layer

polymers, namely shape memory polymers, LCPs exhibit reversible photome-chanical behaviors (see Fig. 10.8a). However, the poor film-forming characteris-tics and mechanical properties of LCPs severely limit their practical applications. In order to overcome this issue, a strategy to use a bilayer structure composed of LCPs and normal polymer plastics, e.g. polyethylene (PE), polycarbonate (PC) and silicone, was developed [56]. In this bilayer structure, LCP is an active layer that provides reversible photomechanical response and the photo-inert plastics is a passive layer that supplies engineered excellent film-forming and mechanical properties (see in Fig. 10.8b). Adhesion between the active layer and passive layer is important for the reversible photomechanical behavior of the bilayer structure and ultimately for the reliability and stability of soft actuators based on this approach. Thus, adhesive interlayers and crosslinking between film layers are ways usually used to enhance the mechanical connection between the active layer and the passive layer. A variety of soft actuators with sophisticated structure have been designed based on the bilayer configuration and will be well described in the next section.

10.4.1 Optically Controlled Switching

In general, optically controlled switching circuits have been realized through photosensitive properties such as resistance that can translate light signals into electrical ones. Compared to the traditional light-sensitive properties, the revers-ible photodeformable behavior mechanism of LCPs is distinct and simple [40]. By incorporation of CNT, the CNT/LCP nanocomposite exhibits unique reversible photomechanical behavior and excellent overall conductivity due to the templating and high conductivity of CNTs respectively. When the nanocomposite strip is irradiated with UV light from the right side, it quickly bends to the left side, i.e. away from the UV source, to contact the left conductive wire making the left electric circuit path continuous. Removal of the UV source allows the

Fig. 10.9 Application of the electrically conductive CNT/LCP nanocomposite strip for a remote electric switch. Reproduced with permission from [40]. Copyright 2013
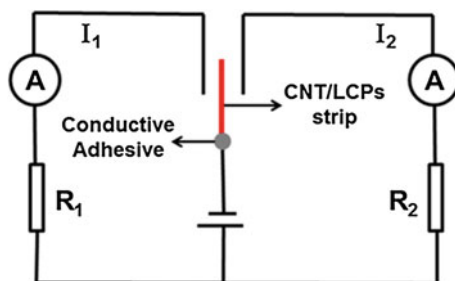
nanocomposite strip to return to its initial position and the electric circuit at the left is open. Similarly, when the nanocomposite strip is UV irradiated from the left side, it quickly bends to the right side to contact the right conductive wire making the right electric circuit path complete, which is similarly reversible. Based on this demonstration of a photo regulation mechanism through LCPs, it can be clearly seen that CNT/LCP nanocomposites can effectively act as optically controlled switches (Fig. 10.9). Moreover, reliability and stability of this optical controlled switching is promising because the photomechanical behavior of the nanocomposite exhibits no decay even after one hundred cycles.

## 10.4.2 IR-Triggered Artificial Arm

As mentioned above, simple and reversible photoinduced bending behavior has been achieved in LCPs by phase transition or change of mesogenic ordering in the LCP microstructures. However, active origami structures usually exhibit complex three dimensional (3D) shapes upon exposure to an external stimulus in environment. Thus, the realization of complex 3D shapes in LCPs could be a key step in enabling their practical application. From Fig. 10.10, it can be observed that distinctive 3D shapes occur upon IR irradiation when different macroscopic structures of soft actuators are designed based on the bilayer structure of CNT/LCP nanocomposite and polycarbonate (PC) [46]. The artificial arm, a most important part of robot, has been drawing extensive attention in the literature and new approaches are continuously being developed. An IR-triggered artificial arm has been successfully fabricated based on CNT/LCP nanocomposites/PC bilayer, for example. In comparison to other artificial arms developed by conducting polymers, dielectric elastomers and shape memory polymers, it needs no electric wire and can grip irregularly shaped objects in different conditions, even in water. This kind of artificial arm can be remotely and accurately controlled and has wide potential applications especially in the aeronautics and astronautics fields.
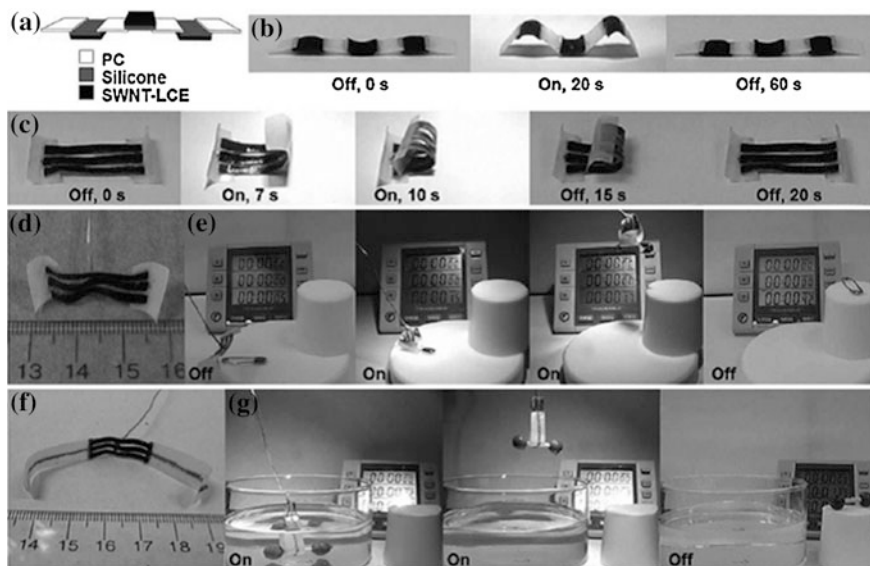
Fig. 10.10 a Macroscopic structure and **b** complex 3D folding behavior of the device composed of bilayer structure CNT/LCPs nanocomposite and PC. **c** Reversible folding and unfolding behavior of the artificial arm based on CNT/LCPs nanocomposite and PC. **d–g** Grip irregular shape objects with this artificial arm in the condition of air and water. Reproduced with permission from [46]. Copyright 2013

10.4.3 Inchworm Walker Devices

Inchworm, an interesting and typical movement mode of active origami, also can be reproduced based on the bilayer structure of CNT/LCP nanocomposite and PC [46]. In general, the structure of active origami exhibiting inchworm movement is complicated. In some cases, sophisticated structures composed of four different layers are required to imitate the inchworm movement in the inchworm walker device (Fig. 10.11b). The movement of the inchworm walker device is enabled by the reversible photomechanical behavior of CNT/LCPs combined with the macroscopic structure of the inchworm walker device. The device bends away from the light source exhibiting an arc shape upon IR irradiation. Due to the unique shape of the bottom PC layer and friction interaction between the bottom PC layer and the substrate, the device then apparently creeps forwards a distance as it completely recovers to its initial shape after the IR source is removed. Because of the reversible photomechanical behavior of CNT/LCPs, the inchworm walker device can creep forward continuously as long as it undergoes an on-off cycle of light irradiation.
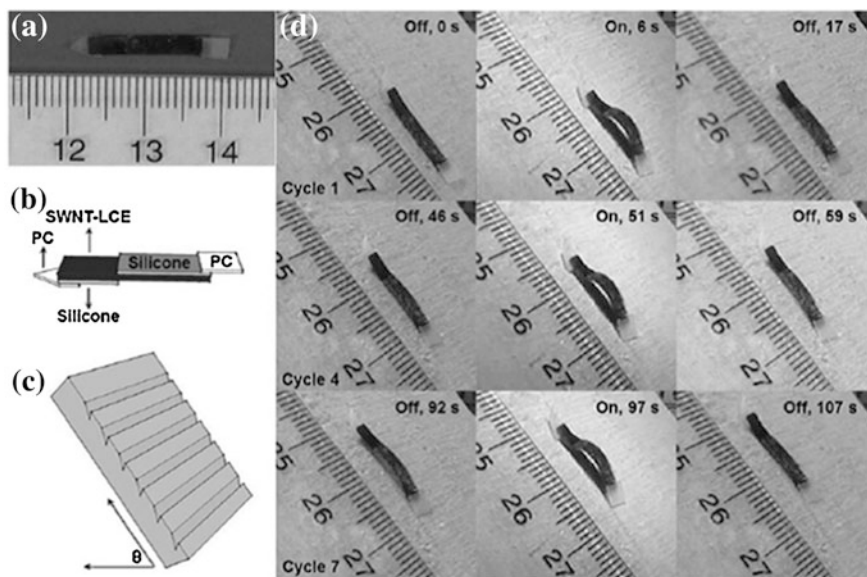
Fig. 10.11 **a** Photograph and **b** macroscopic structure of the inchworm walker device. **c** Scheme of a ratcheted wood substrate. **d** The process of creep behavior of the inchworm walker device during cycles of IR on and off. Reproduced with permission from [46]. Copyright 2013

10.5 Conclusions and Outlook

It is the elegant combination of self-organization properties of LCs with mechanical performance of organic polymers that enables photoresponsive LCPs to directly convert light energy into mechanical work. These kinds of LCPs with their unique characteristics show potential applications in light-driven sensors, actuators and micro-opto-mechanical systems (MOMs). From the viewpoint of practical applications, many characteristics of these devices based on LCPs including the triggering wavelength, complex 3D shape changes and various mechanical functions must be accurately controlled. In order to meet these requirements, self-assembled nanostructures and nanomaterials have been utilized as the template to induce the alignment of mesogens and brought the active components together to render LCPs with new functionality. A variety of excellent soft actuators including optically controlled switching, an IR triggered artificial arm and inchworm walker have been developed based on these LCP nanocomposites. Although the photodeformable behavior of LCPs can be greatly influenced by the incorporation of nanomaterials, the interactions between LCPs and nanomaterials, and the relationship of the self-assembled nanostructure with these interactions, the photomechanical behavior of these systems continues to be explored with considerable effort. Furthermore, a variety of actuators with complicated deformation behaviors based on LCPs nanocomposites are urgently

required for diverse applications. The photoresponsive behavior in such systems can be activated quickly and with high energy transfer efficiency. Several of these new routes have been initiated only during the last few years and some may develop into highly successful research fields and applications. In most of the areas discussed here, the community is still at a relatively early stage of exploration. Undoubtedly, the technical impact of the various themes will be assessed in the coming years. Ultimately, these are very exciting research developments for photodeformable LCPs and nanomaterials, which shed light both on their utility and on the complex, fundamental interactions within these nanostructured and responsive nanocomposites.

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