Photothermal Actuators

# Photothermal Surface Plasmon Resonance and Interband Transition-Enhanced Nanocomposite Hydrogel Actuators with Hand-Like Dynamic Manipulation

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Hydrogel actuators represent a powerful tool due to their ability to capture, move, and be manipulated, which has applications in diverse fields. The development of hydrogel actuators capable of localized movement, where only a part of the whole system moves, wireless remote control, and flexible shape-changing is critical and challenging to fulfill their potential. Here, photothermal hydrogel actuators are designed and fabricated to accomplish a precise hand-like manipulation of encapsulating and finger-like one-by-one bending by light. A thermoresponsive poly(N-isopropylacrylamide) (PNIPAm) active layer and a non-thermoresponsive poly(acrylamide) passive layer are combined to generate a thermal-expansion coefficient mismatch among the interface and this energy eventually transforms into a bending motion. As an energy transformation agent, the gold nanoparticles doped in the PNIPAm hydrogel absorb the light energy and transform it into thermalenergy effectively as a result of a surface plasmon resonance electron-phonon process and intrinsic interband transitions. The resulting nanocomposite actuators exhibit flexible, reversible motions and local hand-like finger flexion driven by either flood illumination or local irradiation. The developed programmable actuators are expected to be an attractive candidate for the next generation of "smart" soft robots.

## 1. Introduction

As one of the most promising intelligent materials, hydrogel materials can dramatically change their volume or other properties upon the trigger of chemical or physical stimulus, such as humidity,<sup>[1–3]</sup> heat,<sup>[4–7]</sup> light,<sup>[8–12]</sup> electric field,<sup>[13–17]</sup> and so on. In the last decade, hydrogels have been demonstrated to be appealing for applications in the field of biomedicine, such as vehicles for

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drug delivery,<sup>[18,19]</sup> matrices for bioseparations, etc.<sup>[20,21]</sup> In recent years, hydrogel actuator, as new type device, receives extensive attention due to distinct advantages: mimic human functionality, adaption in aqueous environments, simple designs, and potential applications in various fields, including biology,<sup>[22]</sup> medicine,<sup>[23,24]</sup> microfluidics,<sup>[25,26]</sup> and robotics.<sup>[27]</sup>

Among the stimuli-responsive actuators, light-driven actuators are particularly attractive devices. Light enables the rapid on–off switching and higher spatial and temporal resolution than other stimuli. Furthermore, light as a stimulus enables facile operation with removing complex step of installing wire. Until now, two main strategies have been developed for fabrication of actuators with light stimulation. As one strategy, photoirradiation-induced ionization/isomerization of chromophores enables the majority of light-driven actuators, in which the size change of azobenzene,<sup>[28–31]</sup> spiropyran,<sup>[32,33]</sup> diarylethene,<sup>[34]</sup>

and so forth<sup>[35]</sup> leads to motions of the actuators. However, these cited instances of ionization/isomerization reaction were limited by slow actuation kinetics, no significant deformation, or narrow selection of efficient spectral range.

Another important strategy is introducing photothermal nanoparticles into thermoresponsive matrices, which undergo a reversible and significant volume change exceed certain temperature. Hauser et al. demonstrated transformations from a single flat gel sheet to buckled shapes due to local photothermal shrinking under light irradiation.<sup>[36]</sup> In addition, light-induced poly(N-isopropylacrylamide) (PNIPAm) bilayer hydrogel actuators have been widely reported. In the study of Zhang et al., graphene oxide-poly(N-isopropylacrylamide) (PNIPAm) nanocomposite and PNIPAm nanocomposite bilayer gels change the isotropic volume contraction into a simple bending deformation.<sup>[37]</sup> In the study of Zhou et al., they generated a simple holistic movement.<sup>[38]</sup> Up to now, light-driven actuator can achieve wireless remote control operation using photothermal transformation agent, but a local operation and flexible shape change still absent. Here we fabricated gold nanoparticles (AuNPs)-doped PNIPAm light-driven actuators that could rapidly undergo arbitrary, flexible, and fully programmable of



local deformation. PNIPAm hydrogels undergo a reversible and significant volume reduction above the lower critical solution temperature (LCST) of about 32 °C.<sup>[39]</sup> AuNPs exhibit surface plasmon resonance (SPR) light absorption because 6s electrons in the conduction band for AuNPs correlated with the electromagnetic field of the incoming light cause collective oscillations of the electron gas.<sup>[40-42]</sup> Besides their plasmon resonances, these plasmonic noble metal nanoparticles also have strong absorption on the high-energy due to intrinsic interband transitions.<sup>[43]</sup> When the two are coupled, sample illumination through exposure to light at wavelengths that coincide with the NPs absorption maxima allows for photothermal heat generation.[44-46] and provides a means to locally raise the hydrogel temperature above the LCST in small, defined areas. In our study, the actuator combined AuNPs-doped PNIPAm film as active layer and poly(acrylamide) (PAAm) as passive layer exhibited remote-control and reversible motions drove by either flood illumination or local irradiation. Especially, a flexible shape-changing, hand-like dynamic manipulation, one-by-one finger flexion was achieved under local irradiation. Compared to the study of Wang et al.,<sup>[47]</sup> we use more simple and common materials to accomplish the same flexible hand-like joint actuation. They created light-driven actuator by combining reduced graphene oxide (rGO) nanosheets and elastin-like polypeptides (ELPs). ELPs need to be recombinantly produced protein-based polymers based upon repeating sequences of the pentapeptide. A broader challenge is that rGO need to be modularly encoded as functional motifs into ELPs backbones using genetic engineering. In our work, we use mature, commercially purchased materials to accomplish the same rapid, flexible, and reversible motions.

## 2. Results and Discussion

Here, to achieve bending motions of actuators upon light exposure, we prepared hydrogel bilayers comprising nanocomposite hydrogel PNIPAm as the active layer and PAAm as the passive layer via a layer-by-layer strategy, as illustrated in **Figure 1**a. First,



**Figure 1.** a) Schematic illustration of the layer-by-layer method for the fabrication of a bilayer-type photoactuator. b) TEM images of 4 nm AuNPs. c) FDTD simulated electric field distribution of the isolated AuNPs with diameter of 4 nm The electromagnetic field |E| enhanced 2.7 times and absorption is enhanced by  $2.7^2 = 7.29$  (electromagnetic field intensity). d) Schematic illustration for the volume shrinking of the hydrogels containing AuNPs under irradiation of light.



a radical polymerization of NIPAm monomer-AuNPs mixture was carried out in water between two glass coverslips with a spacing of 150 µm. After polymerization of the first hydrogel sheet, the top glass slide was removed from the hydrogel sheet. Next, a pregel solution of AAm was injected into a similar mold with a spacing of 100  $\mu$ m, but the top coverslip was replaced by the first nanocomposite hydrogel layer. After 1 h gelation, the nanocomposite hydrogel bilayer was obtained. Finally, the film was cut to arbitrary dimensions and was swollen in buffer solution to equilibrium state. To achieve photothermal transformation, the light absorption AuNPs were synthesized. The synthesis of AuNPs was carried out in air by mixing AuPPh<sub>3</sub>Cl and capping ligand in an organic solvent. Tertbutylamine borane complex was then added to the solvent and stirred until the reduction was accomplished. We use this facile one-step one-phase synthetic route to obtain gold nanoparticles with a narrow size distribution around 4 nm (Figure 1b).

When small spherical gold nanoparticles are irradiated by light, the interband transition excitated resonantly originating from the d band, which relates closely to the low-lying atomic orbital combined with a little intraband absorption originating from the optical response of conduction electrons in the particles. The intensively absorbed radiation is converted into heat efficiently and rapidly as result of electron–phonon process. We use the finite-difference time-domain method (FDTD) to estimate the electromagnetic enhancement of AuNPs (permittivity and the electric susceptibility of gold was chosen from material data of Chemical Rubber Company (CRC) handbook of chemistry and physics) (Figure 1c). Electric field was found enhanced 2.7 times at the border of 4 nm AuNPs, which indicates that the absorption is enhanced by  $2.7^2 = 7.29$  assisted with the plasmonic-mediated effect. The heat created by SPR and interband transition absorption of AuNPs combined with the thermal deswelling of PNIPAm hydrogels could be utilized to trigger the deformation of single nanocomposite gel film (Figure 1d).

The effect of thicknesses ratio of the layers on rolling behavior was studied for bilayer actuator by following the curvature. In Figure S1 (Supporting Information), we show that the curvature normalized by the total thickness reaches its maximum point when the thickness ratio is around 0.6 and decreases again afterward. A reminiscent behavior with zero curvature for the extreme thickness ratios of 0 (passive layer only) and 1 (active layer only) together with a maximum in between occurs in hydrogel bilayers under light illumination. So we fixed the thickness ratio at 0.6 to carry the next experiment. Optical images of single nanocomposite layer and hydrogel bilayer just released from the spacers, at equilibrium states and at deswelling states are shown in **Figure 2**, in which  $h_1$  and  $h_2$  describe the



**Figure 2.** Optical images of a,b,e,f,i,j) single nanocomposite hydrogel and c,d,g,h,k,l) AuNP–PNIPAm/PAAm hydrogel. a–d) Just released from the mold and e–h) at equilibrium swelling states in water at room temperature and i,j) at deswelling states in water at 45 °C. " $h_1$ " and " $h_2$ " represent the thicknesses of PNIPAm layer and PAAm layer, respectively.



thicknesses of the PNIPAm layer and the PAAm layer, respectively. Small (centimeter scale) squares were tailored from the polymerized gel sheets and submersed in a buffer solution expanding to one and a half times the length of the original ones. With the temperature of buffer solution rising, the small square began to shrink. When the temperature reached 45 °C and was kept constant for 10 min, the square from the single layer led a 70% decrease in the volume compared to the initial equilibrium state before heating. While, we can see from the side view that the bilayer square spontaneously rolled into a tube due to internal stress. The PNIPAm layer presents a color of dark red brown, while the PAAm layer is nearly colorless. Both two types of films are uniform and transparent, and the combine of two layers is excellent because the monomer of acrylamide gel was allowed to diffuse into the PNIPAm network, forming PNIPAm–PAAm interpenetrating networks.

On the basis of the photothermal effect of AuNPs, the performance of the PNIPAm–AuNPs film responding to visible light was investigated, and pure PAAm film was carried out for comparison. A ration of size reduction of the films was calculated under light irradiation. The ration of a side length of the active PNIPAm–AuNPs film substantially declines from 1.00 to 0.62 in response to visible light illumination, however the side length of the passive PAAm layer remains steady (Figure S2b, Supporting Information). Due to the inhomogeneous internal swelling, the stress at their common boundary can easily induce bending deformations of hydrogel actuator in response to radiation. **Figure 3**a explains the light-driven bending actuation



**Figure 3.** a) Schematic illustration of the actuation mechanism responding to visible light. b) Optical photos of the PNIPAm–AuNPs/PAAm actuator without light irradiation (left panel) and with light irradiation (150 mW cm<sup>-2</sup>, right panel) for 25 s. c) Curvature ( $\kappa$ ) changes of the actuators. d) Repeatability test of the PNIPAm–AuNPs/PAAm actuator for 10 cycles under visible light irradiation. e) Curvature of an actuator as a function of the irradiation power f) curvature of an actuator as a function of temperature change. The dimensions of the actuator were 30 mm × 3 mm × 235  $\mu$ m (length × width × thickness).



mechanism schematically. When the PNIPAm-AuNPs/PAAm actuator is irradiated by visible light, the photonic energy is absorbed by the AuNPs trapped in hydrogel network. Due to nonradiative relaxation of excited states, the absorbed photonic energy is rapidly converted into thermal energy, to bring out a temperature enhancement of the hydrogel matrix. Therefore, the absorption of visible light leads to a remarkable deswelling of the PNIPAm-AuNPs film. By contrast, the PAAm film is inert to temperature change and no responsive to light. We have also conducted a control experiment about photo-induced bending of PNIPAm/PAAm actuator without AuNPs to verify the effects of AuNPs (Figure S3, Supporting Information). As the PNIPAm-AuNPs composite layer and the PAAm layer were tightly combined, the actuator showed an obvious bending toward the PNIPAm-AuNPs side. When the light source suddenly disappeared, PNIPAm-AuNPs film will release heat to cold environment, resulting in swell of the film. The double laver actuator gradually recovered to the initial state. The photos of Figure 3b show that we grasped one fixed end of the actuator by a thin-tipped tweezer to make it suspending in a buffer solution. When the light was turned on, the actuator showed a giant bending actuation in 24 s. The curvature was up to 4.28 cm<sup>-1</sup>, as shown in Figure 3c. When the light was turned off, the actuator recovered to the vertical state. The curvature ( $\kappa$ ) of the composite bilayer actuator is defined as the inverse of the radius of the actuator at a specific time. Figure 3c shows that the curvature went up quickly with increase of light irradiation time. However, the descending speed of curvature was much slow than the increasing speed. The disparity of increasing speed and descending speed can be explained as follows. In the process of illumination, heat released from every little gold nanoparticle can be conducted to the polymer coating to cause deswelling. Nevertheless, in the process of cooling, heat can only diffuse into the water through the surface of the actuator. The sum of the AuNPs surface areas is several orders of magnitude larger than that of one long actuator. As a consequence increasing speed was much higher than descending speed. A reproducibility test result of the light-driven actuation behavior is shown in Figure 3d. The bending motion was successively repeated for 10 cycles by irradiating the actuator with visible light for 30 s and then kept away from radiation for a further 90 s to recover. The maximum values of the curvature remained stable after several times, confirming good repeatability of the actuation movement. In this study, not only time dependence but also irradiation power dependence has great influence on the experiment. In view of the difficulty of the actuator temperature measurement in water, we measured the relationship between temperature and curvature along with the relationship between curvature and irradiation power separately. The hydrogel actuator in water was placed in a quartz holder and exposed to visible light and monitored with digital camera. As shown in Figure 3e, the actuator presented increasing degree of bending under the increasing irradiation power of white light for 30 s. Figure 3f shows that the curvature of the actuator appeared linearly proportional to the water temperature. These results show that the bending motion of the bilayer actuator composed of PAAm and PNIPAm-AuNPs could both be driven by irradiation and hot water, and temperature change of the actuator were determined by the intensity of irradiation power.

By means of slightly increasing the amount of crosslinker from 2.62 to 5.24 mg in PAAm film, a bilayer photoactuator with a bidirectional bending ability was fabricated. When the actuator was places into the water at room temperature, the swelling ratio of PNIPAm-AuNPs layer is larger than PAAm layer leading to the bending toward PAAm layer into a ring at the beginning. With the illumination time increasing, PNIPAm matrix started to shrink which caused the mismatch strain between both layers decrease and the annular actuator start to unfold gradually. When the swelling ratio in PNIPAm side was equal to the other side, the actuator is straight completely. As the shrink degree further increase, the actuator bent in the opposite direction like a bow. At the end the actuator bent to a reversed ring, toward the PNIPAm-AuNPs layer. Optical graphs of the deformation process are showed in Figure 4a and the whole bidirectional bending motion only lasted for 40 s. In order to identify this bidirectional behavior was not cause by the rising temperature of the water under flood illumination, we attempted to manipulate the hydrogel actuators locally (Figure 4b). Three fabricated circular actuators were placed side-by-side in a culture dish full of water. We shielded the two actuators on two edges against the radiation while only exposed the center region to visible light for 40 s. As a consequence, the light-driven reverse bending behavior only occurred in the irradiated region, whereas those in the shadow showed no change. This phenomenon reveals that the heat used for driving the actuator just induced by the photothermal effect not by the water conduction.

In view of the distinguished bidirectional bending performance of the PNIPAm–AuNPs/PAAm actuator, we further designed and fabricated a flower pattern consisting of six long actuators. The first photo in Figure 4c displays the initial state of the pattern. After the flower was illuminated by visible light (150 mW cm<sup>-2</sup>) for 90 s in room temperature, the petals gradually stretched to flat state, which imitated a blooming process of the flower. With the irradiation time increasing, the blooming flower started to fold reversely toward the PAAm side. The last photo in Figure 4c shows the final state of the flower pattern after illuminated by the visible light for 150 s. The dynamic blooming and folding process is shown in Movie S1 (Supporting Information).

Moreover, based on the bending characteristic, the PNIPAm– AuNPs/PAAm hydrogel sheets can be further cut into different shapes for encapsulating substances as soft manipulators. Five pieces of hydrogel bilayers were tailored into hand shape for encapsulation of small rubber blocks. The hand-shaped PNIPAm–AuNPs/PAAm actuators were put in the buffer solution, and small rubber blocks were put onto the palms. When the hand shape actuators were irradiated by the visible light for 5 min, all the hydrogel palms bent toward the PNIPAm–AuNPs side and rolled into hydrogel tubes, and thus rubber blocks are encapsulated (**Figure 5**a; Movie S2, Supporting Information).

Our hand-shaped matrix can be easily driven by either flood illumination or local irradiation. As certification, the "fingers" of a hand-shaped matrix was irradiated by a blue laser (700 mW cm<sup>-2</sup>) to create flexible joint movement (Movie S3, Supporting Information). Unlike polymer actuators in prior studies bending positions of which need to be predefined and fixed during the manufacture process, any position along each







**Figure 4.** a) Optical graphs of the bidirectional bending motion depending on the irradiation time, b) optical graphs for circular actuators by irradiation with visible light in a selected region (dotted square denotes the light irradiation region). c) Images of a group of long actuators in bidirectional bending motion.

finger could be chosen to serve as a "joint" to show a fully reversible bending motion.

We created nanocomposite hydrogel actuators that exhibit diverse mechanical motions by controlling their shape and surface patterns and by modulating laser positioning, timing, and movement. As a demonstration, we patterned a hand-shaped matrix (Figure 5b) and sequentially irradiated its "fingers" to create joint-like flexing motions. We could bend the fingers in arbitrary order and any position along each finger could serve as a "joint." Therefore, unlike previous polymeric actuators, bending positions did not need to be predetermined and fixed during the synthesis process.







Figure 5. Controlled motion of hydrogel actuators. a) Encapsulation of small rubber blocks in hand-shaped hydrogel sheets. b) Images of the fingers of a hand-shaped hydrogel bending and unbending in response to the location of a laser spot.

#### 3. Conclusions

In this study, we successfully synthesized a series of light responsive hydrogel actuators by radical polymerization of N-isopropylacrylamide (NIPAm) with AuNPs and AAm as the photothermal conversion agent. The AuNPs in the PNIPAm layer absorbed light energy and transformed it into thermal energy rapidly and effectively interband transition and SPR absorption. These bilayer hydrogel actuators presented a large responsive swelling ratio and good reproducibility of the bending motion. The excellent bidirectional bending property, which is obtained from increasing the amount of crosslinker in the PAAm layer, is rapid, reversible, and repeatable. More broadly, our actuators demonstrate to have a sitespecific, hinge-like bending through the precise control of a laser not limited by preprogrammed patterns within the material. Such sensitive and flexible PNIPAm-AuNPs/PAAm hydrogels are proposed to be ideal candidates in many applications, such as remote light-controlled devices, soft robotics, and artificial muscles.

#### 4. Experimental Section

*Materials*: Triphenylphosphine (PPh<sub>3</sub>), mercaptoundecanoic acid, tert-butylamine borane, NIPAm, methylene bisacrylamide (BIS), *N*,*N*,*N*',*N*'-tetramethylethylenediamine, acrylamide (AAm), sodium

acrylate, and ammonium persulfate were purchased from Sigma-Aldrich. Tetrahydrofuran (THF), ethanol, chloroform, and methanol were obtained from Beijing chemical works. HAuCl<sub>4</sub> was obtained from Shanghai chemical research. All reagents were of analytical grade and used without further purification.

AuNPs Synthesis: AuPPh<sub>3</sub>Cl could be synthesized in the form of white powder by reacting HAuCl<sub>4</sub> with PPh<sub>3</sub> in ethanol. Mercaptoundecanoic acid-capped gold nanoparticles were prepared as follows: 0.2475 g (5 equiv.) of AuPPh<sub>3</sub>Cl was dissolved in 50 mL of 1:1 ethanol: chloroform solution. Then, 0.183 g (10 equiv.) of mercaptoundecanoic acid was added to a conical flask, followed by heating (55.2 °C water bath), and finally, 0.435 g (50 equiv.) of tert-butylamine borane was added in the flask. The color of the solution darkened gradually and became purple-red after stirring at 55.2 °C for 2 h. The AuNPs were purified by three precipitationcentrifugation cycles: the solution was precipitated with THF, centrifuged (10 000 rpm, 10 min), and redissolved in 5 mL of methanol.

*Preparation of PNIPAm–AuNPs Hydrogels*: The hydrogel firms containing AuNPs were prepared by mixing 0.24 g mL<sup>-1</sup> aqueous solution of NIPAm monomer (1.48 mL), 0.1 g mL<sup>-1</sup> aqueous solution of sodium acrylate (0.305 mL), 0.02 g mL<sup>-1</sup> aqueous solution of BIS (0.194 mL), and 0.5 mg of dried AuNPs. The mixed solution was polymerized by adding 10 μL of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine and 20 μL of ammonium persulfate solution(0.1 g mL<sup>-1</sup>). The resulting solution was immediately injected into molds formed with two coverslips separated by a spacer of 150 μm. The gelation lasted for 1 h.

*Preparation of Double-Layered Hydrogels*: Bilayer actuators composed of a PNIPAm–AuNPs layer and a PAAm layer was prepared by a layer-bylayer strategy. The first layer was prepared by the same procedure for



the single hydrogel firm, as described in the previous section. The thickness of the spacers used for fabrication of PNIPAm–AuNPs was 150 µm. After gelation of the first hydrogel layer for 1 h, the coverslip was removed from the hydrogel composite. Next, a similar mold was made as above (with a 100 µm spacer) but without the top coverslip. A pregel solution of AAm was injected into the mold and the first hydrogel layer was rolled over to cover above it. The PAAm hydrogel layer was fabricated with 100 µL of pregel solution contained 24 mg g of AAm and 2.62 mg of BIS. Free radical polymerization was initiated by adding 0.5  $\mu$ L of *N*,*N*,*N'*.tetramethylethylenediamine and 1  $\mu$ L of ammonium persulfate solution (0.1 g mL<sup>-1</sup>) to the degassed pregel solution. After gelation, the coverslips and spacers were removed from the composite hydrogel bilayer, and the hydrogel was then swollen in buffer solution (pH 7.3, 0.1 m NaCl).

*Light Manipulation*: A high power metal halide bulb (E27, Sijifeng, Zhejiang) supplied white light irradiation; the intensity of the light was 150 mW cm<sup>-2</sup>, as measured using the full spectrum of optical power tester (Jingyi Optoelectronics Technology Co., Ltd, Guangdong). All the hydrogels were put in a transparent quartz holder with buffer solution (pH 7.3, 0.1 M NaCl) at 25 °C for more than 30 min to reach the full swelling state before every dynamic bending experiment. To create flexible joint movement "fingers" of a hand-shaped matrix, a small hand-held blue laser (Luban, Shanghai) was used and the intensity of the light was 700 mW cm<sup>-2</sup> (411 nm). The whole dynamic bending process was recorded by a digital camera.

*FDTD Simulation*: The simulation was carried in FDTD solutions software. Au material data of CRC handbook of chemistry and physics were used in the simulation, such as the permittivity and the electric susceptibility of gold. The simulation used the fixed excitation wavelength (520 nm), which was close to the gold absorption band. The refractive index of the ambient water medium is 1.33. The deeper red color in the simulation results indicates higher electric field values.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

dynamic manipulation, hydrogels, interband excitation, photothermal actuators, surface plasmon resonance

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