Fabrication of Light-triggered AuNP/CNC/SMP Nano-Composites

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Cellulose, an abundant natural polysaccharide, can be applied to immobilize particles on the surface due to the presence of ample hydroxyl groups. A series of different sizes and contents of gold nanoparticles (AuNP) were prepared on cellulose nanocrystal (CNC). The obtained AuNP/CNC nanocomposites were then blended with shape-memory polyurethane (SMP) to prepare light-triggered AuNP/CNC/SMP nanocomposites through solvent conversion and a solution casting method. The nanocomposite films were endowed with higher mechanical properties and striking remote-control light-triggered shape-memory properties. Moreover, the CNC in the composites also enhanced the photothermal effect of AuNPs by preventing the aggregation of AuNPs. At the same time, the content of AuNPs with existing CNC had a stronger effect on the elevated temperature (ΔT) and the shape-memory properties of films in comparison to the size of the AuNPs.

Keywords: Nanocellulose; Gold nanoparticle; Shape-memory polyurethane; Photothermal effect

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INTRODUCTION

Shape-memory polyurethane (SMP) can change from a temporary shape to a "remembered" permanent shape when exposed to external stimuli, such as heat, light, ultrasound, electricity, or magnetic field. Most stimuli types are based on the stimulus-introduced thermal effect, specifically, the origin of the shape-memory effect of the polymer triggered by the heat. When SMPs are processed above a transition temperature, such as a glass transition temperature (T_g), the polymer generally changes from glassy to rubbery (Reit *et al.* 2014). Compared with traditional heating, *i.e.*, warming of the surroundings or heating the polymer directly, the above-mentioned indirect stimuli remotely activates the local selected shape-memory effect to obtain spatial control of the SMP behavior. This extends the application of SMP in sensors, actuators, micro-optic devices, *etc.* (Chan *et al.* 2016). The laser is one of the many well-known stimuli and a particularly appealing choice. The convenient and most common way of fabricating light-triggered SMPs is to add some nanofillers with photothermal effect properties to the SMPs matrix. One of the most intriguing nanofillers is gold nanoparticles (AuNPs), which exhibit a noteworthy photo-thermal effect (*i.e.*, the conversion of light energy to heat) because of the AuNP surface plasmon resonance (SPR) properties.

Considering the aggregation characteristics of AuNPs caused by Van der Waals attractive forces (Rance *et al.* 2010) and, especially, the negative consequence of AuNP aggregation for the photothermal effect, the homogeneous dispersion of AuNP in matrices becomes a non-trivial issue. Furthermore, the stable AuNP colloidal suspension is almost synthesized in an aqueous phase; nevertheless, the SMP is dissolved in an organic phase.

Therefore, many researchers have focused on how to disperse these AuNPs within a hydrophobic matrix uniformly, while keeping the AuNP monodispersed. For example, Zhang and Zhao (2013) uniformly dispersed AuNPs in chloroform by polycarlactone-functionalized modification of the AuNPs and then prepared the optically-triggered shape-memory composite material. Besides the miscellaneous chemical modification of AuNPs, some researchers propose a green method for the synthesis and stabilization of AuNPs (Kim 2012; Chiu and Huang 2013; Chen *et al.* 2015). In this method, CNC is used as a stabilizer and template agent to prepare CNC-functionalized AuNP (AuNP/CNC) and to prevent AuNP aggregation. The prepared AuNP/CNC nanocomposites have been applied to catalysis (Chen *et al.* 2015), biomedicine (Chiu and Huang 2013), or electronic devices (Kim 2012).

Inspired by the above-mentioned studies, this study focuses on using AuNP/CNC as bifunctional fillers within SMP. However, AuNP can act as a light-triggered heater to remotely and locally control the shape of SMPs. In contrast, CNC can act as a reinforcer, due to its high stiffness and high modulus, and enhance the mechanical properties of SMP. Also, CNC is acting as a stabilizing agent for AuNP. In addition, a new solvent conversion method was proposed for the transferring of AuNP/CNC nanocomposites to the organic solvents. The effect of the AuNP content, size, and CNC on the properties of SMP were investigated, which provides a theoretical basis for research of the wide application of AuNP/CNC nanohybrids in polymers.

EXPERIMENTAL

Materials

Cotton linters with a moisture content of 8% were supplied by Fumin Chemical Fiber Co. Ltd. (Shandong, China). The shape-memory polyurethane elastomer (SMP) was purchased from Lixin material manufacture (Guangdong, China). Sulfuric acid (H_2SO_4, 98 wt.%), cetyltrimethyammonium bromide (CTAB), N,N-dimethylformamide (DMF), acetone, gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), and sodium citrate (Na_3Cit) were of analytical grade and purchased from the Guangzhou Chemical Reagent Factory (Guangzhou, China). All chemicals were used without further purification.

Methods

Preparation of CNC

The CNCs were isolated from the cotton linters through acid hydrolysis as previously mentioned (Zhou *et al.* 2012). The cotton linters were immersed in 64 wt.% sulfuric acid solution with a ratio of 1 g/mL to 8.75 g/mL at 45 °C under strong continuous stirring for 1.5 h. The obtained hydrolyzed cellulose was repeatedly washed, via centrifugation (10000 rpm, 10 min) at least 3 ×, and dialyzed against deionized water until the pH of the suspension was near neutral. Finally, the suspension was ultrasonicated for 5 min at room temperature to obtain a uniform CNC dispersion that was subsequently stored at 4 °C for further experiments.

Preparation AuNPs and AuNP/CNC nanocomposites

The compounds Na_3Cit (0.1M) and $HAuCl_4$ (0.2Mm) were added in molar ratios of 3.5, 2.5, 1.5, and 0.9 to the designated CNCs. The mixtures reacted at 100 °C to obtain AuNP/CNC nanocomposites. The size of the AuNP in nanocomposites was 15 nm, 23 nm,

30 nm, and 40 nm, respectively. The related nanocomposite was denoted as AuNP/CNC-a, nanocomposites with different concentrations of AuNP were prepared by adjusting the dose of the CNC to obtain the nanocomposites of 3 wt.%, 5 wt.%, 7 wt.%, 10 wt.%, and 20 wt.% AuNPs, which were denoted as AuNP/CNC-3, AuNP/CNC-5, AuNP/CNC-7, AuNP/CNC-10, and AuNP/CNC-20, respectively. There were also 30 nm sized AuNPs prepared without any CNC *via* the same method which served as controls.

Preparation of AuNP/CNC/SMP films

A small amount of cetyltrimethylammonium bromide (CTAB 0.2 M) was added to the prepared AuNP/CNC, AuNPs, and CNCS solutions, respectively. The mixing solution was stirred for 30 min and then washed *via* centrifugation (12000 rpm for 20 min, 4 °C). The precipitate was dispersed in acetone by ultrasonic treatment for 20 s to remove residual water and CTAB. Finally, dimethylformamide (DMF) was used to disperse the precipitate *via* an ultrasonic treatment.

Approximately 20 wt.% SMP dissolved in DMF was mixed with the above-mentioned AuNP/CNC suspension with magnetic stirring for 6 h under ambient conditions. The resulting mixtures were subsequently cast into circular polytetrafluoroethylene (PTFE) molds (6 cm in diameter) and oven-dried at 80 °C for 8 h. A series of Au/CNC/SMP nanocomposite films were prepared by changing the above prepared CNC, AuNP, and AuNP/CNC nanocomposites. The contents of the CNC, AuNPs, and the diameter of AuNPs in the Au/CNC/SMP films are shown in Table 1.

Table 1. The Contents of CNCs, AuNPs, and Diameter of AuNPs in the Au/CNC/SMP Films

Sample	AuNP Content in Films (wt.%)	CNC Content in Films (wt.%)	Diameter of AuNP (nm)
SMP	0	0	--
CNC/SMP	0	5	--
Au/SMP-7	0.35	0	23.06± 2.50
Au/CNC/SMP-3	0.15	5	23.06± 2.50
Au/CNC/SMP-5	0.25	5	23.06± 2.51
Au/CNC/SMP-7	0.35	5	23.06± 2.52
Au/CNC/SMP-10	0.5	5	23.06± 2.53
Au/CNC/SMP-20	1	5	23.06± 2.54
Au/CNC/SMP-a	0.35	5	15.33± 2.16
Au/CNC/SMP-b	0.35	5	23.06± 2.50
Au/CNC/SMP-c	0.35	5	30.15± 5.55
Au/CNC/SMP-d	0.35	5	39.16± 5.95

Particle size is averaged over 100 nanoparticles on TEM image.

Characterization of CNC, AuNP, AuNP/CNC, and Au/CNC/SMP Films

The UV-visible absorption spectra from 400 nm to 800 nm were obtained on an Agilent Technologies HP-8453 spectrophotometer (Karlsruhe, Germany), using deionized water as blank. The morphologies and sizes of the gold nanoparticles were recorded using transmission electron microscopy (TEM) (H-7650, Hitachi, Tokyo, Japan) operating at 80 kV accelerating voltage. The mechanical testing (tensile modulus, tensile strength, and elongation at break) of the Au/CNC/SMP films was performed on a Universal material-testing machine (Instron 5567, Boston USA) with a 100 N load cell. The films were cut

into rectangular specimens with 10 mm × 40 mm × film thickness. An average value of at least five replicates for each sample was taken. The photo-thermal conversion properties of the films were tested using a 532 nm green diode laser with a power density of 1.6 W/cm^2 (Changchun New Industries Optoelectronics Technology Co., Ltd., Changchun, China) and a thermometer (UNI-T 1310, UNI-T Electronic Corp, Dongguan, China).

RESULTS AND DISCUSSION

Characterization of AuNPs and AuNP/CNC Nanocomposite

In this paper, AuNPs with a series of different diameters were synthesized by varying the initial molar ratio between Na_3Ct and $HAuCl_4$. Based on the original nucleation-growth mechanism, the rising concentration of the reducing reagent (Na_3Cit) causes an increase in the AuNPs nucleation rate and the initial number of the nuclei (Nguyen *et al.* 2010). Thus, the final size of the AuNPs decreased as the initial number of the nuclei increased after all of the fixed monomers were consumed. Figure 1 shows the UV-vis spectra for the AuNP obtained at various $Na_3Cit/HAuCl_4$ ratios and the red-shift of the SPR wavelength as the $Na_3Cit/HAuCl_4$ ratio decreased, which was indicative of an increase in particle size. The specific size variation of AuNP was observed by TEM (Fig. 1B), and it further demonstrates the different sizes of AuNP that have been synthesized.

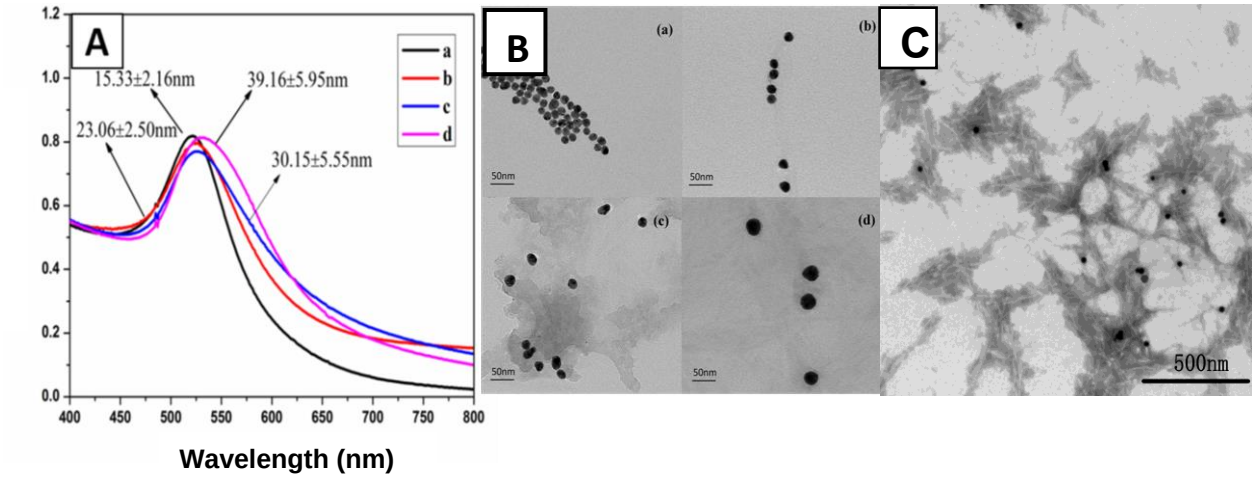

Fig. 1. The UV-vis spectra (A), TEM image (B) of AuNPs prepared using various molar ratios (3.5, 2.5, 1.5, and 0.9) of Na3Ct /HAuCl4 and TEM image (C) of AuNP/CNC with 30 nm size of AuNP

For AuNPs synthesized using the Na_3Cit method in aqueous solution, the citrate acted as a reducing, capping, and stabilizing agent. However, its capping and stabilizing character was very weak. In contrast, during the process of solvent conversion, most of the citrate was removed, which made it very difficult to maintain the AuNPs in a stable monodispersion. This finding is consistent with the results shown in Fig. 2(A); many monodispersed AuNPs aggregated. Compared with the AuNPs without CNCs, the AuNP of AuNP/CNC nanocomposites clearly display monodisperity, as shown in Fig. 2(B). The CNC acted as both a reaction site and a capping agent, distributed around the AuNP, resulting in steric hindrance and preventing AuNP aggregation.

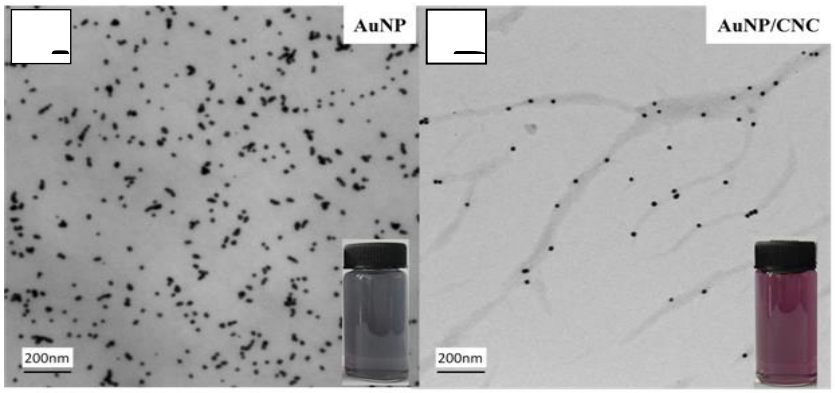

Fig. 2. The transmission electron micrographs and photograph of AuNP (A), and AuNP/CNC (B), dispersed in acetone

Table 2. Mechanical Properties of the Films

Sample	Tensile Modulus (Mpa)	Tensile Strength (Mpa)	Elongation at Break (mm/mm)
SMP	1.73 ± 0.16	19.88 ± 1.26	12.29 ± 0.41
CNC/SMP	2.13 ± 0.03	24.20 ± 1.78	15.40 ± 2.76
Au/SMP-7	1.68 ± 0.06	20.71 ± 2.84	13.45 ± 2.07
Au/CNC/SMP-3	2.28 ± 0.14	23.65 ± 3.04	17.11 ± 2.72
Au/CNC/SMP-7	2.15 ± 0.30	23.40 ± 1.85	18.42 ± 0.26
Au/CNC/SMP-10	2.10 ± 0.37	21.74 ± 2.60	17.43 ± 2.13

Characterization of SMP and Au/CNC/SMP Nanocomposite Film

The mechanical properties of films

Nanocellulose, the primary compositional building block of AuNP/CNC nanocomposites, can be used as a reinforcement or nano-filler to enhance the final mechanical properties of the SMP film. The mechanical properties of pure SMP and nano-composite films with various amounts of AuNP/CNC nanohybrids are summarized in Table 2. In contrast to the neat SMP, the films filled with CNC displayed marked enhancements in the tensile modulus, tensile strength, and the elongation at break. The maximum tensile modulus and tensile strength were 31.79% and 22.73% higher, respectively, than the pure SMP films. The formation of a continuous filler (CNC) network within the SMP creates a tremendous reinforcing effect. In addition, an essential factor affecting the mechanical properties of SMP films is the inherent chain stiffness and rigidity of the CNC from inter- and intra-molecular hydrogen bonding (Lee *et al.* 2004). Moreover, the elongation at break of the SMP with CNC has been improved, reaching the maximum of 18.42 mm/mm from 12.29 mm/mm. Wu *et al.* (2007) and Richardson *et al.* (2011) reported similar observations. The higher extensibility contributed to homogeneous distribution in the SMP matrix, resulting in the strong interaction at the reinforcement SMP interface. Notably, the AuNPs had little impact on the mechanical properties of the films, which may be attributed to their low content.

The Photothermal Effect of Films

The AuNPs in the nanocomposites exhibit a photothermic effect that is dependent on the SPR frequency of the AuNPs. The observed profile of the temperature rising with time under green laser light irradiation (1.6 W/cm^2 532 nm) is depicted in Fig. 3 (A) for

the film blended with a certain amount of AuNP/CNC. The heating rate of the films was fairly fast, and the ΔT reached an equilibrium state within 20 s. The temperature equilibrium of AuNPs in the matrix is dominated by the thermodynamic equilibrium process, including a heat-absorbing process caused by the photothermal effect of AuNPs and a heat-losing process such as convection, conduction, *etc.* (Zhou *et al.* 2012). When the two processes are unbalanced, the ΔT presents either increases or decreases. Figure 3 (B) shows the relationship between the concentration of AuNPs and the ΔT. In theory, ΔT should have a linear increase with an increase in the concentration of AuNP (Cao *et al.* 2015). As expected, the result roughly followed this relationship when the AuNPs content was below 0.35 wt.%. However, there was no further increase at higher loadings, which can be mainly ascribed to smaller inter-AuNPs spacing (D) at higher concentrations. When D is 5 × shorter than the radius of the AuNP, the SPR of AuNP will be weakened as well as the efficacy of the photo-thermic effect (Cortie *et al.* 2007). The comparison between the Au/SMP-7 and Au/CNC/SMP-7 samples showed that the CNC enhanced the photothermal effect of the films by 50%, which may be attributed to the good monodispersion of AuNPs caused by CNCs, as mentioned above.

The effect of the AuNP size on the ΔT is shown in Fig. 3 (C). There was a slight change with the varying size of AuNP. A larger individual gold particle generates more heat due to its high surface area. Jana *et al.* (2001) reported that small size AuNP should transduce energy from light to heat more efficiently than larger nanoparticles. Thus, the small fluctuation in certainty of the scope of ΔT caused by AuNP size is a comprehensive result for many factors such as the number of the AuNPs, the distance between AuNPs in the films *etc.*

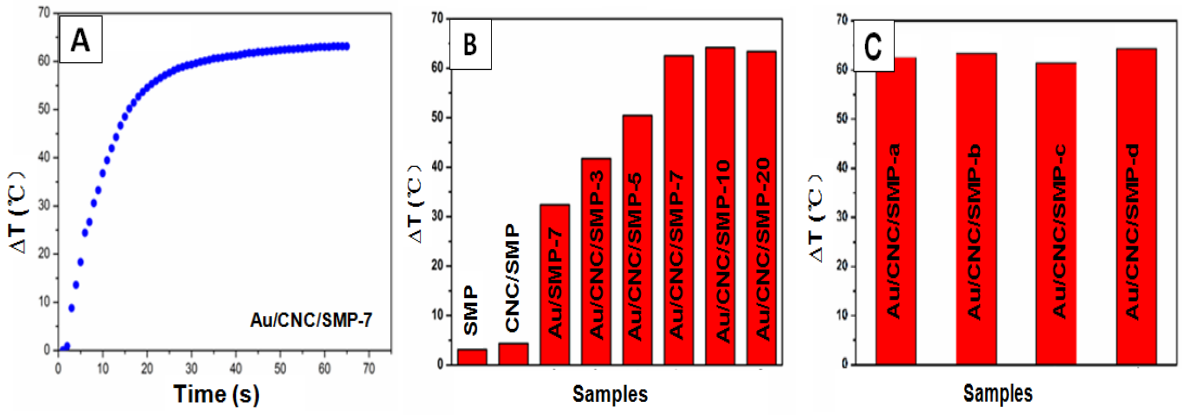

Fig. 3. The temperature profiles (A) of Au/CNC/SMP-7, temperature changes at a steady state in the nanocomposite material as induced by the photo-thermic effect in different contents (B), and the diameter (C) composite of AuNPs films

The Shape-memory Properties of Films

Figure 4 presents the characteristic experimental process from a 532 nm laser driven a single actuation for the Au/CNC/SMP-7 film. An original film was deformed into a fixed shape by folding it at 80 °C, and then allowed to cool for shape fixation. A burst of green light laser (532 nm) struck the fold of film where the strain energy was stored. The film recovered the straight shape recovery within 19 s of the laser exposure. The main mechanism is that the AuNP dispersed in the SMP matrix absorbed the energy of the laser,

ultimately transforming the energy into heat, and then raised the temperature in the fold to above the soft segment T_g of the films, which made the strain energy release.

The aim of this study was to prepare rapid, high-efficiency, and remote-control light-triggered shape-memory material. Therefore, under the laser exposure 1.5 m away from the samples, the shape recovery ratio and shape recovery response time of the films were measured to study the impacts of the AuNP contents, diameter of AuNP, and the CNC in the films on the shape-memory property. Table 3 shows that the response times of the shape-memory decreased with increasing AuNP. The shape recovery ratio of Au/CNC/SMP-3 with 0.15 wt.% AuNP was only 73.2% after 1 min laser exposure, which is consistent with the above mentioned photothermal effect results.

The same explanation applied for the impact of the diameter of AuNP and CNC, which means that the optical-to-thermal energy conversion efficiency of AuNPs directly affected the extent of the shape recovery and response time. The shape memory behavior of composites is highly dependent on the temperature and laser exposure time. Therefore, the higher temperature of the film, the faster it recovers the original shape, the shorter the shape recovery time and vice versa.

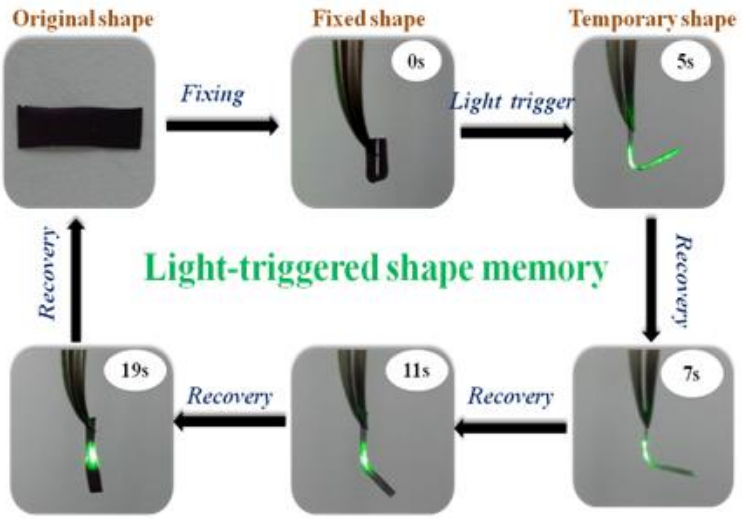

Fig. 4. The process of light-triggered shape-memory for Au/CNC/SMP-7 film

Table 3. The Shape Recovery Ratio of the Films after 1 min of Laser Exposure, and Response Time When the Shape Recovery Ratio Reaching 100%

Sample	Shape Recovery Ratio (%)	Light-triggered Time (s)
Au/SMP-7	77.8	--
Au/CNC/SMP-3	73.2	--
Au/CNC/SMP-5	100	24
Au/CNC/SMP-7	100	19
Au/CNC/SMP-10	100	18
Au/CNC/SMP-20	100	17
Au/CNC/SMP-a	100	18
Au/CNC/SMP-b	100	19
Au/CNC/SMP-c	100	17
Au/CNC/SMP-d	100	16

CONCLUSIONS

1. The cellulose nanocrystal (CNC) acted as a template, dispersant, and stabilizing agent in the manufacturing of AuNPs/CNC by mixing CNC and $HAuCl_4$. For the sake of dispersing these hybrids in the hydrophobic matrix, the prepared AuNP/CNC nanohybrids in the aqueous phase were well displaced into the organic solvent conversion instead of miscellaneous chemical modification of AuNPs.
2. The Au/CNC/SMP films with enhanced, rapid, high-efficiency, and remote-control shape-memory properties were obtained through a solution casting method. Due to the added CNC, the tensile modulus and tensile strength of the Au/CNC/SMP films were 31.79% and 22.73% higher than that of the pure SMP ones. The addition of CNC also prevented the aggregation of AuNP, which enhanced the photothermal effect and shape-memory properties of the films. The concentration of AuNPs is the major factor relating to the photothermal effect and shape-memory property of films, while the diameter of AuNPs has no obvious effect on the properties of films.
3. The resultant AuNP/CNC nanocomposites can be used as an excellent functional agent to enhance the mechanical properties of polymers and to endow the polymer outstanding photothermal effect and light-triggered shape-memory properties, which will further broaden the applications of SMP.

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