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Laser Stimulated Shape Memory Polymer with Inclusion of Gold Nanorod—Effect of Aspect Ratio and Critical Role of On-resonance Irradiation

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Gold nanorods (AuNRs) are excellent photothermal agents to enable a variety of laser stimulated functional polymers. One key issue is to maximize the photothermal conversion efficiency of AuNRs. In this study, the light responsive AuNR/shape memory polymer (SMP) nanocomposites with inclusion of AuNRs of varied aspect ratios were prepared, characterized, and their laser irradiation induced bending behavior was investigated. The critical role of the on-resonance irradiation condition—a close match of the longitudinal plasmon resonance of the AuNR with the wavelength of the incident laser—has been established. It allows for maximizing the photothermal conversion efficiency of AuNRs to result in the rapid and large deformation of the AuNR/SMP nanocomposites. For the AuNR/SMP nanocomposite films prepared under similar processing conditions, the close-to-resonance irradiation at a 1.27 W/cm^2 was able to induce a bending rate of 27°/s and maximum bending angle of 90.4°. In contrast, the off-resonance irradiation at a 1.89 W/cm^2 resulted in negligible response.

1. Introduction

Shape memory polymers (SMPs) are one important type of stimuli responsive polymers that possess dual-shape or multiple shape changing capability[1,2]. This makes them highly valuable for applications spanning various areas, such as switches and sensors, smart fabrics, heat-shrinkable tubes for electronics or films for packaging, self-deployable sun sails in spacecraft, self-disassembling mobile phones, intelligent medical devices, or implants for minimally invasive surgery[3–6]. In addition to the traditional and most commonly adopted direct heating stimulus, the novel SMPs that can respond to, such as, moisture, water/solvent, ions, pressure, light, pH value, and electric current have emerged recently[7–12]. In particular, by taking advantage of the thermal effect of a variety of functional nanoparticles, a new class of SMP nanocomposites with remote triggering capability has received great attention recently. With inclusion of magnetic nanoparticles such as iron (III) oxide nanoparticles[13] and ferromagnetic microparticles[14], the SMPs are able to be triggered for shape changing under inductive heating induced by an alternating magnetic field. By incorporation of gold nanoparticles (AuNPs) into SMP matrix and utilizing their localized surface plasmon resonance (LSPR) enhanced photothermal effect[15,16], the SMP capable of rapid shape-changing response upon laser irradiation has been demonstrated[17,18]. The same approach was recently being adopted for developing high-performance liquid crystal elastomer based micro-actuators[19]. The advantages of AuNPs over some other photothermal agents, e.g., single walled carbon nanotube (SWCNT) and iron oxide[20], are their much higher photothermal conversion efficiency as well as chemical and biochemical inertness[21–23]. For this reason, a very small amount of AuNPs inclusion in a polymer matrix would be able to induce significant temperature rise[19,24].

To achieve optimal photothermal conversion for AuNPs, the wavelength of the stimulating laser must be wisely selected such that it is in resonance with the LSPR of AuNPs. At this condition, the optical absorption cross section, C_{abs}, of AuNPs is several orders of magnitude higher than that at an off-resonance condition. Therefore, it may result in an extremely high photothermal conversion efficiency[25,26]. When using gold nanorods (AuNRs) as the photothermal agents to develop remotely triggered SMPs[20], this resonance matching condition is especially critical, since the longitudinal LSPR of AuNR strongly depends on its size, shape and aspect ratio[22,23,27]. With a wise control of the synthesis conditions to adjust the geometric parameters of AuNRs and therefore the resonance matching

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condition, one may develop laser stimulated SMPs with wavelength-selective capability. Such a capability cannot be realized by using some other photothermal agents such as carbon black and SWCNT that have broadband absorption characteristics. With an inspiration to develop AuNR/SMP capable of wavelength-selective stimulation, in the present study, we prepared light responsive AuNR/SMP nanocomposites through a polyelectrolyte exchange process. By varying the size and aspect ratio of AuNRs, we characterized and investigated the laser irradiation induced bending behaviors of AuNR/SMP nanocomposites. The important role of the on-resonance irradiation condition—a close match of the longitudinal plasmon resonance of the AuNR with the wavelength of the incident laser—has been established. At this condition, the photothermal conversion efficiency of AuNRs can be maximized to enable rapid and large deformation of the AuNR/SMP nanocomposites, which is critical for developing high-performance AuNR enabled laser stimulated functional materials.

2. Experimental

2.1. Synthesis and characterization of AuNRs

AuNRs in aqueous solution were synthesized by following the seeding growth method developed by El-Sayed and Nikoobakht[28]. This method requires preparation of a seed solution and a growth solution separately. In the synthesis, the in-house purified Mill-Q water with resistivity greater than 18.2 MΩ cm was used as the solvent for preparing both the seed and the growth solution. The ascorbic acid (99.7%) was purchased from Fisher Scientific Inc. and the other chemicals were purchased from Sigma-Aldrich Corp and used as-received. In brief, the seed solution was prepared by mixing 5 mL of an aqueous solution of tetrachlorauric acid ($HAuCl_4$, 0.25×10^{-3} mol/L) and cetyltrimethyl ammonium bromide (CTAB, 0.10 mol/L) with 0.3 mL of 0.01 mol/L freshly prepared ice-cold sodium borohydride ($NaBH_4$) solution under vigorous stirring for 30 s. Such prepared seed solution was shielded from light and kept in a 25 °C water bath for 2 h before its use for making AuNRs. The growth solution was prepared first by adding 0.05, 0.1, 0.15 and 0.2 mL of 5.0×10^{-3} mol/L silver nitrate ($AgNO_3$) aqueous solution into a vigorously stirred mixture of 0.1 mL of 0.05 mol/L $HAuCl_4$, 0.075 mL of 0.1 mol/L ascorbic acid ($C_6H_8O_6$) and 10 mL of 0.1 mol/L CTAB at 25 °C. The amount of $AgNO_3$ was varied to tailor the aspect ratio of the AuNR. To initiate the growth reaction of AuNRs, 0.06 mL seed solution was mixed with the as-prepared growth solution and the mixture was kept in dark and incubated in a water bath at 28 °C for 12 h. It has been observed that, with increasing the amount of $AgNO_3$, the color of the AuNR solution varied from purple to red.

An exchange process developed by Murphy et al. [29] was used to avoid the aggregation issue when incorporating AuNRs into polymer matrix. In the exchange process, the CTAB coating of AuNRs is replaced by a layer of polyelectrolyte. This would allow a transfer of the as-prepared AuNRs in aqueous solution into an organic solvent DMF and therefore facilitate their incorporation into SMPs without aggregation. In brief, the above as-prepared AuNR aqueous dispersion was centrifuged at 2000 r/min for 10 min by using Optima MAX Ultracentrifuge (Beckman Coulter Corp.). Subsequent to centrifugation, the supernatant was carefully removed and the precipitate was re-dispersed in DI water using a Bransonic 2510 bath sonicator (frequency of 37 kHz). This centrifugation and re-dispersion were repeated twice to remove the excess CTAB. Two different polyelectrolytes, poly(allylamine hydrochloride) (PAH, MW ~ 15,000 g/mol) and poly(acrylic acid, sodium salt) (PAA, MW ~ 15,000 g/mol) were used for exchange operation. To this CTAB removed AuNR aqueous dispersion (1 mL), 0.2 mL polyelectrolyte of concentration 10 mg/mL in a 1×10^{-3} mol/L NaCl solution and followed by 0.1 mL of 0.01 mol/L NaCl were added. The mixture was shaken for 30 min to complete the exchange process. After this exchange process, the excess polyelectrolytes were removed by centrifugation to give pelletized AuNRs. Such obtained AuNR pellet could readily be dispersed in dimethylformamide (DMF). The centrifugation and re-dispersion process were applied twice to remove residual water to ultimately result in AuNR/DMF dispersion ready for use in preparing AuNR/SMP nanocomposite.

A Varian Cary 5000 UV–vis–NIR spectrophotometer was used to acquire the UV–vis-NIR spectra of the AuNRs prepared above to confirm their successful formation. A JEOL JEM-ARM200cF Transmission electron microscopy (TEM) was used to acquire their size information. The UV–vis-NIR spectra of the AuNR/DMF dispersion acquired at a series of diluted concentration: $C = 1/2\times C_0$, $1/3\times C_0$, and $1/5\times C_0$ were used for estimating the gold concentration, where C_0 is the AuNR concentration in the as-prepared AuNR/DMF dispersion. This was done by utilizing Beer's law: $Abs = C_{ext}Cl$, where l is the optical path length equal to 0.5 cm and C_{ext} is the extinction cross-section of AuNR. C_{ext} was calculated according to a numerical simulation package MNPBEM developed by Hohenester et al. [30] based on boundary element method[31].

2.2. Preparation, characterization, and laser irradiation of AuNR enabled SMP nanocomposite films

The commercially available SMP, Tecoflex EG-72D (Lubrizol Corp.), was used as the polymeric matrix for fabricating AuNR/SMP nanocomposites. EG-72D is a cycloaliphatic poly (ether urethane) copolymer, which is composed of poly (tetramethylene glycol) (PTMG) as soft segment, methylene bis (p-cyclohexyl isocyanate) (H12MDI) as hard segment, and 1, 4-butanediol (BD) as the chain extender[32,33]. To prepare the EG-72D/AuNR nanocomposite films, a 2 wt% solution of EG-72D in DMF was prepared first at an elevated temperature of 150 °C under argon atmosphere. To this solution, an appropriate amount of AuNR/DMF dispersion was then added and mixed to give the EG-72D/AuNR/DMF ternary dispersion with the Au concentration (relative to the polymer) controlled at ~0.1 wt%. A subsequent casting and solvent evaporation protocol (80 °C in vacuum for 24 h and 120 °C in vacuum for another 24 h) was applied to result in the AuNR/SMP nanocomposite films. The UV–vis-NIR spectra of the as-prepared AuNR/SMP films were acquired by a Varian Cary 5000 UV–Vis–NIR spectrometer to examine the dispersion states of AuNRs.

To investigate the laser irradiation behavior of the AuNR/SMP nanocomposite, the as-prepared composite film was programmed to a temporary shape first. This was done through a manual stretching in hot water bath (70 °C) followed by a fixation process in iced water. In the stretching process, a draw ratio of 3.5 was used and the width of the stretched AuNR/SMP strips was controlled such that it is greater than the laser beam size.

A ThorLabs diode laser assembly (L808P200-808 nm in wavelength + LTC100-B LD controller kit) was used for performing the laser irradiation of the stretched AuNR/SMP nanocomposite film. The laser beam size was estimated to be 3.5 mm × 3.5 mm = 12.25 mm^2 and the laser power density received by the film sample was adjusted in the range of 1.27–1.89 W/cm^2. During the laser irradiation process, the motion of the composite film was videoed at 25 frames per second and the video was used for quantitative analysis of the shape changing behavior of the film.

3. Results and Discussion

With varying the amount of $AgNO_3$ used in the seed-mediated growth method, the aspect ratio of the AuNR can be readily adjusted. This has been clearly confirmed by the UV–vis–NIR spectra

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