Research Article

Ka-Wai Yeung, Yuqing Dong, Ling Chen, Chak-Yin Tang*, Wing-Cheung Law, Gary Chi-Pong Tsui, and Daniel S. Engstrøm

Printability of photo-sensitive nanocomposites using two-photon polymerization

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Abstract: Two-photon polymerization direct laser writing (TPP DLW) is an emerging technology for producing advanced functional devices with complex three-dimensional (3D) micro-structures. Tremendous efforts have been devoted to developing two-photon polymerizable photo-sensitive nanocomposites with tailored properties. Light-induced reconfigurable smart materials such as liquid crystalline elastomers (LCEs) are promising materials. However, due to the difficulties in designing two-photon polymerizable liquid crystal monomer (LCM) nanocomposite photoresists, it is challenging to fabricate true 3D LCE micro-structures. In this paper, we report the preparation of photo-sensitive LCE nanocomposites containing photothermal nanomaterials, including multiwalled carbon nanotubes, graphene oxide and gold nanorods (AuNRs), for TPP DLW. The printability of the LCE nanocomposites is assessed by the fidelity of the micro-structures under different laser writing conditions. DLW of GO/LCM photoresist has shown a vigorous bubble formation. This may be due to the excessive heat generation upon rapid energy absorption of 780 nm laser energy. Compared to pure LCM photoresists, AuNR/LCM photoresists have a lower laser intensity threshold and higher critical laser scanning speed, due to the high absorption of AuNRs at 780 nm, which enhanced the photo-sensitivity

Ka-Wai Yeung, Yuqing Dong, Wing-Cheung Law, Gary Chi-Pong Tsui: Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

of the photoresist. Therefore, a shorter printing time can be achieved for the AuNR/LCM photoresist.

Keywords: two-photon polymerization, direct laser writing, 3D nanofabrication, photothermal nanomaterials

1 Introduction

In recent years, advanced functional devices with threedimensional (3D) micro-structures have attracted enormous attention due to the enhanced functional density, performance and efficiency [1]. To facilitate the progress of research, micro-fabrication techniques such as inkjet printing [2], photolithography [3] and selective laser sintering [4] have been developed. Devices such as sensors [5], micro-capacitors [6] and micro- and nanoelectromechanical systems [7] have been produced for biomedical and energy storage applications. With the increasing demand for device miniaturization, as well as the growing interest in plasmonic metamaterial applications [8,9], conventional additive manufacturing technologies are no longer viable due to their limited resolution at the micron scale [10]. Two-photon polymerization (TPP) lithography is a promising direct laser writing (DLW) technique due to its true 3D fabrication capability and high spatial resolution [11]. Photosensitive materials made of reactive monomers or oligomer and photo-initiator can be polymerized upon the two-photon absorption at the laser focal spot. Therefore, by utilizing a femtosecond near-infrared (NIR) laser source, a complex 3D structure with submicron resolution (~100 nm) can be achieved. Currently, most studies are focusing on developing new two-photon polymerizable composite materials with a variety of tailored properties, such as biocompatibility [12] and magnetic properties [13], for TPP DLW. By incorporating functional nanomaterials into the polymer matrix, scaffolds for cell cultures [14], photonic crystals [15] and micro-current collectors [16] have been produced.

^{*} Corresponding author: Chak-Yin Tang, Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China, e-mail: cy.tang@polyu.edu.hk, tel: +852 2766 6608, fax: +852 2362 5267

Ling Chen: Manufacturing, CSIRO, Private Bag 10, Clayton South, Vic 3169, Australia

Daniel S. Engstrøm: School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, LE11 3TU, Loughborough, UK

Liquid crystalline elastomers (LCEs) are soft materials that contain mesogenic moieties with self-organization capability [17]. These materials can respond to external stimuli such as heat with a macroscopic shape change owing to a nematic-to-isotropic phase transition of the mesogens. This reconfigurable property of LCEs is promising for the development of advanced actuating, sensing and robotic devices [18]. Recently, light actuation of LCE nanocomposites has been developed by introducing organic and inorganic nanomaterials, such as carbon nanotubes (CNTs) [19], graphene oxide (GO) [20] and gold nanorods (AuNRs) [21], into the LCE matrix. By exploiting the photothermal or surface plasmonic effect of the nanofillers, which transform photon energy to heat [22], photo-actuation can be achieved. Devices based on light-actuated LCE nanocomposites have been considered as "smart" due to their capability of remote and on-demand activation through the use of clean energy. However, despite extensive research [23] on LCE-based devices, most of them are fabricated through soft lithography and thus only 2D or 2.5D simple structures, which limit the performance of the device, have been reported. Although TPP may offer an alternative way for 3D micro-/nano-fabrication, to the best of our knowledge, there has been only limited report on producing two-photon polymerizable photosensitive nanocomposites for producing LCE microstructures [24]. This may be due to the challenges including the design of TPP-compatible liquid crystal monomer (LCM) photoresist, as well as poor miscibility between the photothermal nanomaterials and the polymer photoresist matrix.

In this study, we prepared three LCM-based photosensitive nanocomposites by addressing the aforementioned difficulties by using two-photon polymerization direct laser writing (TPP DLW). Two-photon polymerizable LCM photoresist was made by using LCM, a cross-linker with acrylate moieties, and a photoinitiator with an absorption window of 300-400 nm. Different photothermal nanofillers, including multiwalled CNTs, GO and AuNRs, were synthesized and prepared. To improve the miscibility, surface functionalization of CNTs and AuNRs was used. The printability of the nanocomposites with different nanofillers prepared by TPP DLW was studied in terms of the structural fidelity, which was assessed through morphological observation. The writing parameters were also determined through a parametric sweeping function. Finally, by harmonizing the laser writing parameters, TPP DLW of 3D LCE nanocomposite microstructures was successfully achieved.

2 Experimental section

2.1 Materials

Multiwalled carbon nanotubes (MWCNTs, purity >98%) with lengths less than 2 µm and diameters of 10-20 nm were purchased from Nanotech Port Co. Ltd, China. Pyrolytic graphite (PG), phosphorus pentoxide (P_2O_5) and hydrogen peroxide (H₂O₂) were supplied by Sinopharm Chemical Reagent Co. Ltd, China. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), hexadecyltrimethylammonium bromide (CTAB, 98%) and 3-mercaptopropionic acid (MPA) were purchased from Macklin, China. Potassium persulfate (K₂S₂O₈), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), sodium borohydride (NaBH₄, \geq 96%) silver nitrate (AgNO₃) and Irgacure 369 were supplied by Sigma-Aldrich, USA. Hydroquinone (99%) was purchased from Tokyo Chemical Industry Co. Ltd, Japan. 4-Bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene (RM257) and 4-methoxybenzoic acid 4-(6-acryloyloxy-hexyloxy)phenyl ester (C6BP) were supplied by SYNTHON Chemicals GmbH and Co KG, Germany.

2.2 Preparation of photothermal nanomaterials

Photothermal nanomaterials including MWCNTs, GO and AuNRs were prepared separately. MWCNTs were first functionalized using concentrated sulfuric acid (H₂SO₄) and nitric acid (HNO₃) with a volume ratio of 1:3 to improve their dispersibility. The suspension was refluxed at 80°C for 10 h. After being cooled down, the solution was diluted with excess deionized (DI) water followed by filtration. The acid-treated MWCNTs were dried at 50°C in a vacuum for 12h and redispersed in acetone.

GO was obtained by using Hummer's method [25] via oxidation and ultrasonic stripping. First, 3 g PG, 2.5 g $K_2S_2O_8$ and 2.5 g P_2O_5 were stirred in 24 mL of H_2SO_4 (98%) at 80°C for 5 h. After being cooled down to room temperature, 500 mL of DI water was added to the mixture and stirred for another 10 h. The preoxidized product was collected by filtration of the mixture. Six grams of dried pre-oxidized product and 3 g NaNO₃ were mixed in 240 mL of H₂SO₄ at 5°C. Then 20 g KMnO₄ was slowly added and the temperature was maintained at 5°C. The solution was then stirred for 2h at 40°C. followed by an addition of 250 mL of DI water. The temperature of the solution was raised to 98°C for 15 min. The reaction was stopped by adding 500 mL of DI water and 20 mL of 30% H₂O₂ solution. After being continuously stirred for 2h, the solution was washed using 1000 mL of 5% HCl aqueous solution and the mixture was filtrated. The washing and filtration processes were repeated five times until the solution becomes neutral. Brown colored graphitic oxide was obtained and dried under vacuum. GO was obtained by exfoliating the graphitic oxide using ultrasonication. Graphitic oxide powder was first redispersed into ethanol. Then, the suspension was allowed to sonicate for 2h. Finally, monolayer GO was obtained with a concentration of 6 mg/mL. AuNRs were synthesized via a modified seedmediated growth method [26]. In brief, 0.5 mM HAuCl₄ solution and 0.15 M CTAB were mixed in a volume ratio of 1:1 under vigorous stirring. After the solution became clear, 0.01 M NaBH₄ solution was slowly added to the solution until the solution turned light brown. The stirring lasted for 2h to yield the seed solution. The growth solution was prepared by mixing 10 mL of HAuCl₄ solution (10 mM), 200 mL of CTAB (0.1 M), 1.5 mL of AgNO₃ solution (0.1 M) and 10 mL of hydroquinone solution. The growth of AuNRs was initiated by adding 2.5 mL of seed solution into the growth solution. The reaction was aged for 12 h, followed by washing with DI water and centrifugation at 12,000 rpm for 10 min to remove excess reactance. The as-synthesized AuNRs were redispersed in DI water. Thiol functionalization of AuNRs was utilized to avoid aggregation of AuNRs in the LCM photoresist [27], by adding 0.5 mL of MPA ethanol solution (1% v/v) to the freshly prepared AuNR suspension under vigorous agitation at 35°C for 4 h. The mixture was then placed into a dialysis bag in a beaker of ethanol for purification. MPA-modified AuNRs (MPA-AuNRs) were obtained and redispersed in ethanol prior to use.

Morphologies of the as-prepared MWCNTs, GO and AuNRs were observed using transmission electron microscopy (TEM; Jeol HEM-2001, Japan). The nanomaterials were deposited on TEM copper grids for investigation. A UV-vis spectrophotometer (UV1102; Techcomp Ltd, China) was used to measure the absorbance of the photothermal nanomaterial within a wavelength range of 400–1000 nm.

2.3 Preparation of photo-sensitive nanocomposites

Two-photon printable LCM photoresists were prepared by mixing the monomer C6BP, chiral crosslinking monomer RM257 and photo-initiator Irgacure 369. C6BP and RM256 were first dissolved in acetone in a molecular ratio of 1:9. Then, 2 mol% Irgacure 369 was also dissolved into the LCM acetone solution in a dark environment. The LCM nanocomposite photoresists were prepared by dispersing 1 wt% of MWCNTs, GO and AuNRs in the LCM acetone solution under ultrasonication at 40°C. After solvent evaporation, photo-sensitive nanocomposites, namely, MWCNTs/LCM, GO/LCM and AuNR/LCM photoresists, were obtained for two-photon DLW.

2.4 TPP via DLW

Two-photon DLW of LCE nanocomposite micro-structures was performed using a commercially available 3D laser lithography system (Photonic Professional GT; Nanoscribe GmbH) equipped with an objective lens with a magnification of 63× and a numerical aperture of 1.4. Polymerization of the photoresist was initiated by a 780 nm laser source with a 100 femtosecond pulse duration and 80 MHz repetition rate. Due to the fine laser focal spot, only a small volume (voxel) was polymerized so that structures with submicron resolution were achieved. To realize 3D micro-structures, 3D computer-aided design models were generated and converted into a general writing language, which defines the trajectories of the laser focus, as well as the system parameters during the DLW.

The schematic of the DLW process with an oil immersion configuration is depicted in Figure 1. The LCM nanocomposite photoresist was first prepared (Figure 1a). Before the laser writing process, nanocomposite photoresist printing cells were prepared by using two stacked glass slides, between which there is a glass sphere space (~100 µm diameter; Figure 1b). The cell was maintained at 60°C and infiltrated with the photo-sensitive nanocomposite. The printing was performed in the oil immersion configuration (Figure 1c). Immersion oil was dropped onto the bottom side of the cell. The laser writing process was started and observed by a built-in live camera. The development of the micro-structure was done by immersing the sample in acetone for 1 min in a dark environment, followed by rinsing with isopropanol to remove the unpolymerized photoresist.

2.5 Printability assessments

During the DLW process, the laser dose, which is determined by the laser power and scanning speed, is

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TPP DLW of LCE microstructures (Oil configuration)

Figure 1: (a) Photothermal nanofillers added to the mixture of LCM monomer, crosslinking monomer and photoinitiator to form LCM nanocomposite photoresist; (b) LCM nanocomposite photoresist printing cell assembly; and (c) TPP DLW of LCE nanocomposite micro-structures using femtosecond laser.

vital for sustaining polymerization of the photoresist. The intensity of the laser should be higher than the polymerization threshold. However, if the intensity exceeds the damage threshold, the photoresist may be burnt. As the polymerization threshold varies depending on the photoresist composition, it is important to determine the suitable range of laser parameters for producing good writing quality, i.e., high fidelity.

The printability of the photo-sensitive nanocomposites was assessed in terms of the fidelity of the structures fabricated using different laser parameters. After the development process, the structure must survive without damage. In order to obtain satisfactory quality of 3D micro-structures, it is also important to study the optimal writing condition. This was done through a dose test by using the parametric sweep function in generating a pyramidal structure. A laser power setting of 7.5–22.5 mW and a scanning speed of 1-9 mm/s were used. The critical scanning speed, which is defined as the maximum speed for generating a microstructure without any defect, was also determined. A scanning speed from 1 to 9 mm/s at a fixed laser power of 7.5 mW was chosen. The laser printed micro-structures were observed using a scanning electron microscope (JEOL JSM-6490) at an accelerating voltage of 15 kV. All samples were sputter-coated with a thin layer of gold. The optical images were acquired using a Leica DM 4000 M optical microscope.

3 Results and discussion

3.1 Characterization of photothermal nanomaterials

The morphology of the as-prepared photothermal nanomaterials was characterized using TEM as shown in Figure 2. After dispersing into the LCM matrix, stable nanocomposite photoresists were obtained. No aggregation could be observed. Improvement of the stability of MWCNTs within the LCM photoresist was accomplished by oxidizing the surface of the MWCNTs using a strong acid [28]. After the treatment, the amorphous carbon was removed. This created some surface defects, and the surface was functionalized with carboxylic groups. Compared to that of the as-received MWCNTs, the average diameter of the oxidized MWCNTs was reduced (Figure 2a). The TEM image of the as-synthesized GO is shown in Figure 2b. A large noncrumpled sheet of monolayer GO with a smooth surface and high transparency can be observed. Due to the presence of oxygenated functional groups within the graphitic oxide, it is likely to be exfoliated into monolayer GO using ultrasonication [29]. Figure 2c shows the morphology of the as-synthesized AuNRs. AuNRs with an average width of 13 nm and an aspect ratio of 4.6 were obtained.

Photothermal conversion is crucial for a lightactivated LCE actuator. The photothermal effect of MWCNTs, GO and AuNRs can be categorized into thermal vibration and plasmonic heating. Carbon-based materials convert optical energy into heat through molecular vibration. Within the carbon structure, abundant pi (π) bonds with loosely bonded electrons exist. Thus, a lower energy is required for excitation of the electrons. Under light illumination, these loosely bonded electrons absorb photon energy and excite from π to π^* orbital. Due to the electron-phonon coupling effect, the electrons relax to their ground state. This phenomenon leads to vibration of the atomic lattices, which generates heat and causes the rise in temperature. MWCNTs and GO both exhibit a wide optical absorption over the entire spectrum [30]. The absorption band of the materials depends on the spacing of the electronic levels. In MWCNTs and GO, the abundant conjugated π bonds facilitate the absorption over the entire spectrum. In addition, the large area of 2D carbon materials such as GO also demonstrated higher absorption compared to 1D or 3D carbon-based structures [30]. Moreover, MWCNTs and GO demonstrated good thermal conductivity [31], which is also vital for effective photothermal conversion [32]. Compared to other photothermal materials such as metals and semiconductors, carbon-based materials have the advantages of low cost, wide absorption and good photothermal conversion efficiency [29,33]. These properties make them efficient photothermal conversion materials under different light sources.

Photothermal conversion of AuNRs occurs due to the plasmonic resonance under electromagnetic radiation. In metals, the free conduction electrons absorb electromagnetic radiation and excite to a higher energy level [34]. However, due to the shallow skin depth of metallic materials, absorption of energy takes place only near the surface [35]. At a certain wavelength, localized surface plasmon resonance (LSPR) occurs due to the photon-induced oscillation of electrons, which leads to the formation of hot electrons [36]. The energy of the hot electrons, which is decayed through radiative emission and electrons interactions, results in a photothermal effect. The absorption wavelength of AuNRs mainly



Figure 2: TEM images of the as-prepared (a) MWCNTs; (b) GO and (c) AuNRs.

depends on the size and aspect ratio [37]. Therefore, in order to obtain AuNRs with absorption near 780 nm to enhance the photo-sensitivity of the photoresist [38], the aspect ratio is controlled at about 4.6. The UV-vis analysis of the as-prepared AuNRs is illustrated in Figure 3. The absorption spectra of surface plasmonic AuNRs have demonstrated two LSPR bands at about 510 and 800 nm. During the DLW process, excitation of LSPR in AuNRs may occur, which increases the photosensitivity of the nanocomposite photoresist [38]. This may lower the required energy dose for TPP, and thus printing time can be reduced with a faster laser scanning speed.



Figure 3: The UV-vis spectrum of AuNRs.

3.2 DLW of photo-sensitive nanocomposites

The material selection for the LCM photoresist mainly depends on the optical properties of its constituent. During the DLW fabrication, two-photon absorption takes place within a small voxel at a laser focus. The DLW process utilized a 780 nm laser with two-photon excitation wavelength at 390 nm. A photo-initiator with good absorption at 390 nm is required for an effective TPP. Therefore, in this study, the photo-initiator Irgacure 369 with an absorption window of 300-400 nm was selected. Moreover, the cross-linker used for the photoresist should demonstrate good transparency at the TPP laser wavelength to prevent laser intensity attenuation. RM257 with good optical transparency at 780 nm was chosen [39]. Figure 4 shows a woodpile structure produced using a pure LCM photoresist, which has an overall dimension of $28 \times 28 \times 7 \,\mu\text{m}^3$ with a line spacing of 2 µm and a layer-to-layer distance of 1 µm. Due to the appropriate selection of the materials, successful TPP DLW was demonstrated. The conventional approach in fabricating light-activated LCE actuator is by doping photo-responsive dye into the LCE matrix, such as azodyes [40]. However, these dyes are not suitable for DLW fabrication, owing to the overlap between the absorption peak of the dye (around 350 nm) and the two-photon absorption peak of the photo-initiator [39], which affects the polymerization of the photoresist. As MWCNTs, GO and AuNRs showed minimal absorption at two-photon absorption wavelength, they were chosen as the photothermal nanofillers for the LCM photoresist.



Figure 4: SEM image of the LCE-based woodpile structure.

For DLW fabrication of the woodpile structures using pure LCM, MWCNT/LCM, GO/LCM and AuNR/LCM nanocomposite photoresists, the laser writing parameters, including power and scanning speed, were selected so that the polymerization threshold was reached. Among them, pure LCM photoresist required a higher laser energy to initiate the polymerization. Furthermore, when printing the GO/LCM nanocomposite photoresist, vigorous bubble formation was observed. This may be due to the high rate of photothermal conversion in GO under 780 nm laser irradiation. As GO absorbs the laser energy efficiently [30], excessive localized heat may be generated. Consequently, the local energy absorbed exceeded the damage threshold of the nanocomposite photoresist, leading to vaporization or burning of the photoresist. In this study, the LCM nanocomposite photoresists with 0.1, 0.5 and 1 wt% of GO were studied. Similar results were obtained.

The polymerization threshold of the photoresist mainly depends on its constituent, including the monomer, crosslinker, photoinitiator, and the nanofiller [37]. In this study, the major factor is the optical properties of the photothermal nanofillers. It was found that the polymerization threshold of AuNR/LCM photoresist was lower than that of MWCNT/LCM photoresist with a faster scanning speed at the same laser power setting. Although MWCNTs are efficient photothermal conversion materials, MWCNTs have shown a high absorbance within 300–400 nm [41], which may hinder the two-photon absorption by the photo-initiator [39]. Moreover, the optical absorption of AuNRs near 780 nm was higher than that of MWCNTs. During the DLW process, LSPR effect occurs, thus promoting the photosensitivity of the photoresist [38]. Compared with the MWCNTs/LCM photoresist, the AuNR/LCM photoresist may absorb laser energy more effectively, leading to a faster laser scanning speed and shorter printing time.

3.3 Printing parameters and printability assessments

DLW is capable of producing a complex micro-structure with a high precision and resolution. It is critical to assess the optimal laser writing parameters for efficiently fabricating structures with good fidelity. The laser intensity must be higher than the polymerization threshold of the photoresist, which is defined as the minimum laser intensity for generating the desired features with good structural integrity after completing the development process. It must also be lower than the damage threshold to avoid overexposure, which causes an uncontrollable micro-fabrication with local bubble formation or burning. As the threshold level may be dependent on the photoresist composition, printability assessments are important to achieve the best printing result [42].

In order to study the range of laser writing conditions of pure LCM, MWCNT/LCM and AuNR/LCM photoresists, the parametric sweep function was

employed using different laser powers, ranging from 7.5 to 22.5 mW, and scanning speed, from 1 to 9 mm/s. The laser power range was selected according to the polymerization and damage threshold of the photoresists. A pyramidal structure was used as the printing model. A 4×9 array of the pyramidal structures was generated using different sets of laser writing conditions and observed under SEM, as shown in Figure 5. It was found that the polymerization thresholds of MWCNT/ LCM and AuNR/LCM photoresists are lower than that of the pure LCM photoresist. This may be due to the NIR absorption and the photothermal effect of MWCNTs and AuNRs during the TPP DLW fabrication, which enhances the photo-sensitivity of the photoresist. Among the two LCM nanocomposite photoresists, the AuNR/LCM photoresist demonstrated the lowest polymerization threshold. This is owing to a higher absorbance of the AuNRs within the NIR region compared to MWCNTs [43]. The dynamic range of a successful print, i.e., no deformation or damage observed after development, is also highlighted in Figure 5.

In order to investigate the effect of photothermal nanofiller on the DLW speed, the critical scanning speed was determined. The woodpile structures were printed using the pure LCM and AuNR photoresists under a fixed laser power of 7.5 mW and scanning speed ranging from 1 to 9 mm/s. The printing was repeated three times to assess repeatability. The AuNR/LCM photoresist showed a higher critical scanning speed (9 mm/s) compared with pure LCM photoresist (6 mm/s) due to the enhanced photo-sensitivity. The incorporation of AuNRs into the LCM photoresist speeded up the DLW process, which may significantly reduce the time for mass fabrication. The woodpile structure fabricated using the AuNR/LCM



Figure 5: SEM images of a 4×9 array of pyramidal structures generated using AuNR/LCM photoresist with different sets of laser writing conditions.



Figure 6: SEM images of the AuNR/LCE micro-structure fabricated by TPP DLW: (a) woodpile structure; frame structures of (b) regular dodecahedron, (c) octahedron and (d) pentagon cylinder; and (e) micro-clamps.

photoresist at a critical speed is illustrated in Figure 6a. Based on the aforementioned findings, different microstructures, including regular dodecahedron, photonic structure, frame structures and micro-clamps, were fabricated using the AuNR/LCM photoresist, as displayed in Figure 6b–e.

4 Conclusion

In this study, three photon-sensitive nanocomposites, including MWCNT/LCM, GO/LCM and AuNR/LCM photoresists, have been prepared for TPP DLW. A series of investigations have been conducted to assess the printability of the nanocomposites in terms of the required printing parameter, shape fidelity. During the writing process of the GO/LCM photoresist, excessive energy absorption by GO has led to tremendous heat generation and thus vigorous bubble formation, which in turn hindered the formation of the 3D structure. The results also revealed that the AuNR/LCM photoresist had a lower laser intensity threshold due to the higher absorption of AuNRs at 780 nm compared to CNTs. The AuNR/LCM photoresists also showed a higher critical laser scanning speed, implying a shorter printing time compared to pure LCM photoresists. By optimizing the printing parameters, complex 3D micro-structures have been successfully generated using the AuNR/LCM photoresists. This study provides a better understanding

of photo-sensitive nanocomposites based on photothermal nanomaterials and LCMs.

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