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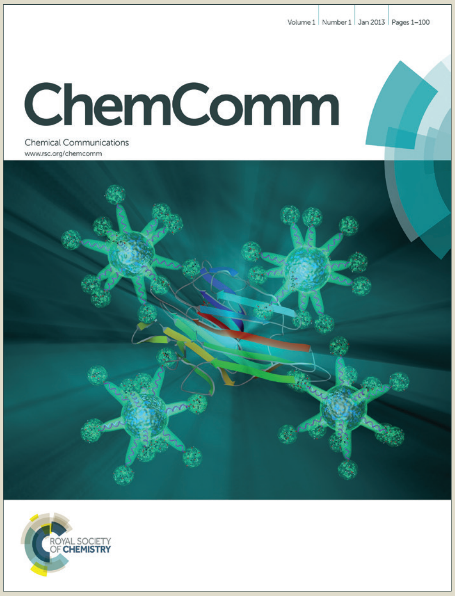

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**COMMUNICATION**

# Near-Infrared-Responsive Gold Nanorod/Liquid Crystalline Elastomer Composites Prepared by Sequential Thiol-Click Chemistry

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**A novel NIR-responsive GNR/LCE composite fiber material is prepared by a three-step sequential thiol-click chemistry approach. Taking advantage of GNRs' significant photo-thermal effect, GNR/LCE composite material with a very low Au loading-level (0.09 wt%), under 808 nm NIR stimulus can achieve the N-to-I transition and shrink dramatically in ambient environment.**

In recent years, light-responsive liquid crystalline elastomers (LCEs), regarded as a new generation of soft actuators and shape-memory materials, have received more and more scientific attentions.[1] As a remote-controlled, precisely-manipulated, clean energy source, light has been used to trigger the disorientation of liquid crystal mesogens. These microscopic structural changes can be further amplified in the crosslinked LCE networks to achieve significant macroscopic deformations of the whole materials. Based on this basic principle, many state-of-art light-driven LCE devices,[2] such as motors,[3] artificial cilia,[4] microrobots,[5] oscillators[6] and 3D microstructures,[7] etc. have been developed.

Most of traditional light-responsive LCEs were designed relying on the *trans-cis* transformation of azobenzene chromophores triggered by ultraviolet irradiation. Recently, visible/infrared (Vis/IR) lights, due to their excellent biocompatibility and high tissue penetration abilities, were applied instead of UV stimulus, as alternative driving forces of novel light-responsive LCEs, which have become a growingly promising research subject in LCE community. The previously reported preparation strategies can be divided into three general categories: 1) the molecular structures of mesogens are particularly designed to absorb high-wavelength light. For example, LCE films bearing mesogens built around the long conjugated azotolane moieties, could perform bending upon exposure to 436-530 nm light irradiation.[8] 2) Inorganic or organic up-conversion materials[9] are incorporated into azo-containing LCE networks to translate near-infrared (NIR) source into low-wavelength light which could be absorbed by azo groups.[10] 3) All other systems are designed in order to make use of the photo-thermal effects, which use "photochemical-to-thermal converters" to transform photons into heat and thus induce the thermal LC-isotropic phase transition of LCE materials.[11] The key benefit of the last idea is that chemists can jump out of "azo-requirement box" to choose a wide variety of mesogens to synthesize LCEs. However, up to now, successfully applied thermal conductive fillers were limited to very few candidates, such as carbon nanotubes, graphene,[11a-h] or plasmonic nanoparticles.[11f-g]

Gold nanomaterials, and in particular gold nanorods (GNR), exhibit unique shape-dependant localized surface plasmon resonance (LSPR) properties[12] which can be tuned to the NIR region and have been applied in a variety of plasmonic photothermal conversion applications, such as photothermal therapy,[13] gene delivery[14] and microfluidic devices.[15] However to the best of our knowledge, there was no any light-driven LCE example using GNRs as thermal conductive fillers, due to two possible technical problems: 1) GNRs are immiscible with organic LCE networks. 2) GNRs aggregate easily, losing LSPR property and the corresponding NIR-responsive effect. To address these obstacles, we herein report a three-step sequential thiol-click[16] approach to stabilize and embed GNRs into LCE networks.

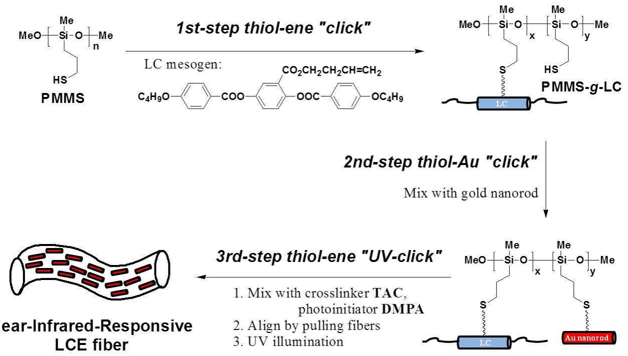

**Fig. 1** Schematic illustration of a three-step sequential thiol-click approach of preparing GNR/LCE composites.

The general design and preparation protocol is shown in Fig. 1. Starting with commercially available poly[3-mercaptopropylmethylsiloxane] (PMMS) which possesses one thiol group in every monomer unit,[17] we first partially grafted mesogenic alkene, (3''-butenyl)-2,5-di-(4'-butyloxybenzoyloxy) benzoate onto PMMS chain by thiol-ene click chemistry, and accurately controlled the graft density (~70 mol%) by feeding PMMS with LC monomers based on a predesigned molar ratio.[18] The leftover unreacted mercapto groups could not only be used to stabilize GNRs *via* Au-S bond but also be engaged in crosslinking reactions.

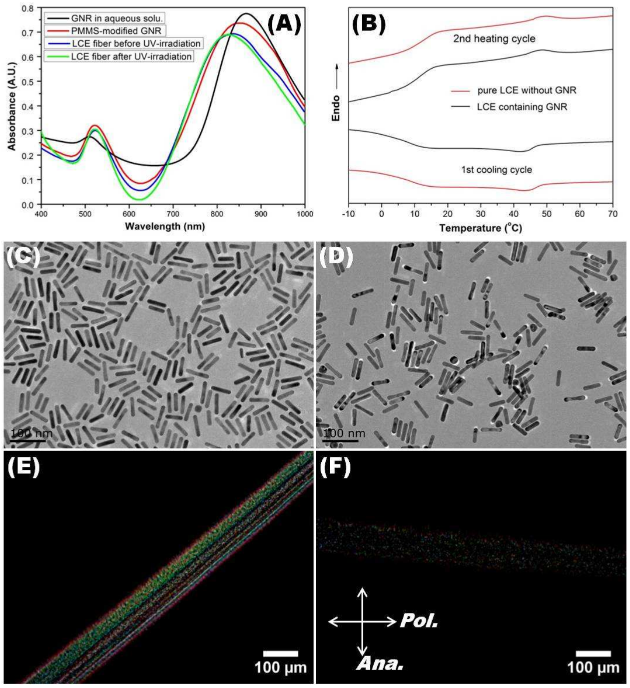

**Fig. 2** (A) UV-Vis spectra of GNR/water solution, GNR/THF solution, GNR/LCE composite samples before and after UV-crosslinking respectively. (B) DSC curves of pure LCE fiber sample and GNR/LCE composite fiber sample. TEM images of (C) GNR/water solution and (D) PMMS-modified GNR/THF solution. POM images of GNR/LCE composite fiber sample oriented at the angle either (E) 45° or (F) 0° to the polarizer.

The second thiol-click step, as the most challenging step, is to efficiently embed GNRs into LC matrix.[19] GNRs were fabricated by a one-pot synthesis protocol using phenol reduction according to literature report.[20] The gold concentration of the obtained GNR-dispersed aqueous solution was measured as $4.77 \times 10^{-2}$ mg/mL by inductively coupled plasma optical emission spectrometry (ICP-OES). As shown in Fig. 2C and Fig. S4, highly monodisperse GNRs (ca. 50~60 nm length, 8~10 nm width) with LSPR peak at 865 nm (Fig. 2A) and transverse plasmon resonance peak at 510 nm were prepared. To transfer the water-soluble GNRs into organic solutions, we chose PMMS as the exchanging ligand of hexadecyltrimethylammonium bromide (CTAB) since PMMS could not only strongly bind to GNRs *via* Au-S bond, but also be highly miscible with **PMMS-*g*-LC** polymer matrix. As illustrated in Fig. S5-7 and Fig. 2D, after the ligand-exchange, organo-soluble GNRs with high dispersion were successfully produced in THF solution, and the corresponding LSPR peak blue-shifted to 850 nm (Fig. 2A), which was caused by a limited GNR aggregation scenario occurring in the ligand-exchange process at the water-oil interface. Finally, the obtained GNR/THF solution was mixed with **PMMS$_{0.70}$-*g*-LC** polymer, the crosslinker triallyl cyanurate (TAC) and the photo-initiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA). The mixture solution was highly stable and precipitates did not appear even after the sample has been stored at ambient temperature for one week.

The above mixture was concentrated to remove any solvents and then heated up to the isotropic phase, The desired GNR/LCE composite fiber was drawn by dipping the tip of a capillary pipette in the melted mixture, and pulling quickly.[21] These fibers are stable for many hours in the LC temperature range. At ambient temperature, where the sample is in its nematic phase, the fibers were irradiated with a 365 nm UV source to perform photo-crosslinking and accomplish the last thiol-click reaction. Compared with GNR/THF solution sample, the uncrosslinked and crosslinked GNR/LCE composite fibers' LSPR peaks slightly blueshift to 830 nm and 827 nm respectively (Fig. 2A), which implies a limited GNR aggregation scenario. The gold weight percentage of GNR/LCE composite fiber was measured as 0.09 wt% by ICP-OES technique (The detailed measurement method is listed in Supporting Information).

We used polarized optical microscopy (POM) to study the alignment in the nematic GNR/LCE composite fibers. As shown in Fig. 2E-F, the fibers present extinction when the fiber long axis is perpendicular or parallel to one polarizer. Rotation of the fiber by 45° maximizes the transmission. Although some defects are observed within the fibers, the uniformity of the alignment is qualitatively excellent. Electron microscopy was further applied to study GNR/LCE composite fiber microstructures since we were very interested in knowing the arrangement of GNR particles dispersed in the LCE matrix: could external pulling force also align GNRs' long axis along the fiber axis orientation? As shown by scanning electron microscopy (SEM) observations, GNRs are absent of the fiber surface (Fig. S8A-B). The internal structure of the fiber was then investigated by slicing thin longitudinal sections (65 nm thick per cut) of fiber with an ultramicrotome.[22] As illustrated in Fig. S8C-D, the orientation of the GNRs is disordered and their distribution is not uniform. This phenomenon might derive from the very low gold concentration (0.09 wt%) and inevitable aggregation behavior.

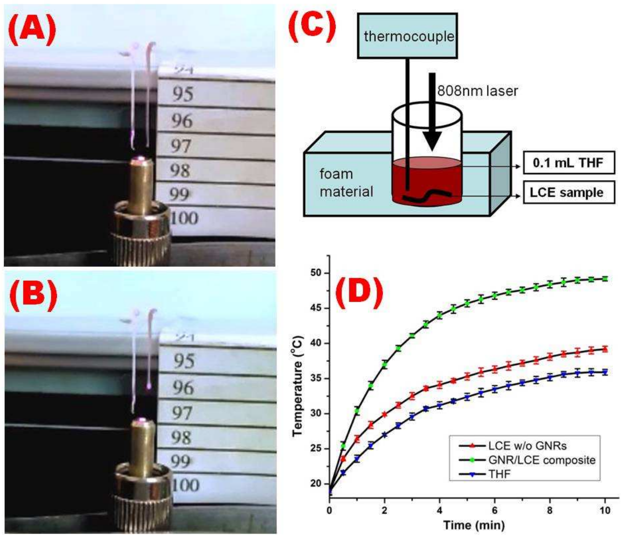

**Fig. 3** An 808 nm laser source has been illuminating on pure LCE fiber (left) and GNR/LCE composite fiber (right) for (A) 0 mins and (B) 10 mins respectively. (C) A schematic illustration of thermocouple experiment of measuring GNRs' photo-thermal effect. (D) A diagram of temperatures of THF reference solutions containing none, pure LCE fiber and GNR/LCE composite fiber respectively vs. NIR illumination time.

The NIR-responsive photo-thermal experiments of GNR/LCE composite fibers were performed using a 808 nm semiconductor laser source. For comparison purpose, we prepared pure LCE fibers without GNRs. As shown in Fig. 3A-B and S1.avi, GNR/LCE composite fibers shrinked under 808 nm NIR illumination for 5-10 min while pure LCE fibers remained intact. We used POM to record the direct imaging of a composite fiber before and after actuation. As demonstrated in S2.avi, the original birefringence of the composite fiber vanished at r.t. after NIR illumination, which implied an obvious N-to-I transition. In order to prove that this shrinking behavior really derived from GNRs' photo-thermal effect and exclude the possibility that the thermal energies directly released by the laser source might solely heat up the LCE samples to above the isotropic phase, we performed two control experiments.

Firstly, we recorded the DSC curves of a GNR/LCE composite fiber and of a pure LCE fiber respectively. As illustrated in Fig. 2B, the two samples have almost exactly same phase transition temperatures (G - 15 ℃ - N - 49 ℃ - I, on heating) although the N-to-I clearing point of GNR/LCE composite fiber is slightly lower (~0.6 ℃). Meanwhile, the N-to-I enthalpy change of GNR/LCE composite fiber is 1.067 $J{\cdot}g^{-1}{\cdot}K^{-1}$ which is similar to the Δ H value (0.980 $J{\cdot}g^{-1}{\cdot}K^{-1}$) of pure LCE fiber. This experiment indicates that the two LCE samples with or without GNRs require relatively equal amounts of heating energy to achieve the N-to-I transition. Thus, if there was no GNRs' photo-thermal effect, pure LCE fiber should have also shrinked as GNR/LCE composite fiber did.

Secondly, we used thermocouple equipments to analyze GNRs' photo-thermal ability. Since the fibers are very thin (100~300 nm), we could not get reliable information of the fibers surface temperature directly, we chose an alternative indirect experiment. We suspended 20.0 mg GNR/LCE composite fiber sample and 20.0 mg pure LCE fiber sample into 0.10 mL THF, respectively. The two fibers suspensions in THF and pure THF reference solution were illuminated by NIR laser source and the temperature rises of these solutions were measured by thermocouple equipments (Fig. 3C). As illustrated in Fig. 3D, after 10 minutes irradiation, the temperature of GNR/LCE suspension was 13~15 degrees and 10~12 degrees higher than those of pure LCE sample and THF blank solution respectively. This scenario further indicates that GNRs' photo-thermal effect is able to raise the temperature of LCE sample to jump over the N-to-I transition.

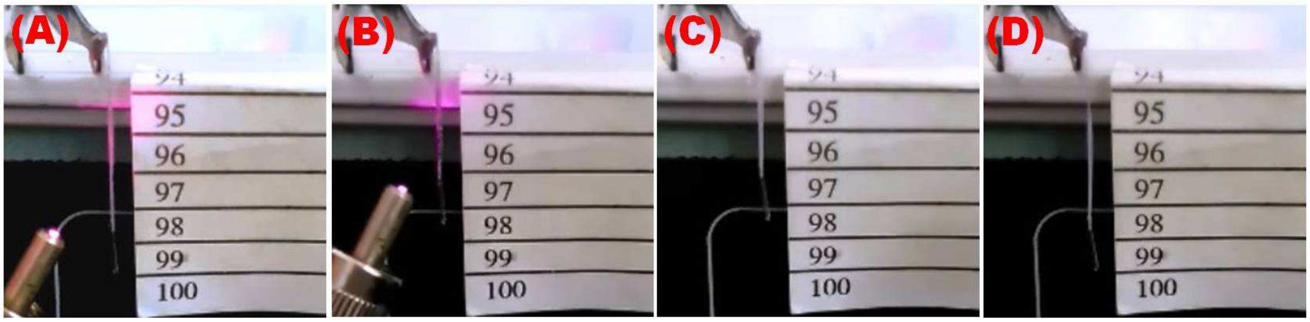

**Fig. 4** An 808 nm laser source has been illuminating on a GNR/LCE composite fiber with a small piece of capillary pipet (ca. 3 mg) load for (A) 0 mins and (B) 10 mins respectively. After removing laser source, the GNR/LCE composite fiber slowly expanded from (C) the shrinked shape to (D) its original length at room temperature in ca. 2 hrs.

After NIR light stimulus was removed, the GNR/LCE composite fibers remained shrinked, and did not spontaneously expand back. Such an irreversible phenomenon was already observed in other LCE fiber materials.[23] Inspired by Zentel's setup,[23c] loading on the fiber a small weight as an external force to stretch up the wrinkled fiber, we glued a small piece of capillary glass pipette (ca. 7.0 mg) on the tail of a GNR/LCE composite fiber after NIR laser source was removed. As demonstrated in S3.avi, the fiber could slowly regain its original length in 1 min at ambient temperature, which is within the nematic phase of this LCE material. However, this GNR/LCE composite fiber could not lift up the glued small piece of capillary glass pipette (ca. 7.0 mg) if we re-illuminated this fiber. Alternatively, we glued another smaller piece of capillary glass pipette with less weight (ca 3.0 mg) on the tail of a thicker GNR/LCE composite fiber. As shown in Fig. 4 and S4.avi, the fiber could lift up this lighter load under NIR stimulus; meanwhile the fiber could regain its original length after the laser source was switch off, although the relaxation time became much longer (ca. 2 hrs).

Besides these above experiments, we also explored in doping a higher concentration of GNRs (ca. 0.47 wt%) into LCE matrix. Compared with the GNR/LCE composite with a 0.09 wt% Au, this new higher Au loading-level sample presented almost exactly same LSPR peak (Fig. S10) and a slightly faster NIR-responsive rate (S5.avi and Fig. S11).

In conclusion, we prepared a novel NIR-responsive GNR/LCE composite fiber material by using a three-step sequential thiol-click chemistry approach. The embedded GNRs could be effectively stabilized by the spare mercapto groups of PMMS-based LCPs and the maximal LSPR peak appears at 827 nm. Taking advantage of GNRs' significant photo-thermal effect, GNR/LCE composite fiber material with a very low Au loading-level (0.09 wt%), can shrink dramatically under 808 nm NIR stimulus at room temperature. Elastomers based upon this system are of potential utility as NIR-responsive actuating materials. Preparation of GNR/LCE composite films and elucidation of the properties of composite materials with different Au loading-levels are under further investigation.

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## Notes and references

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