

Supporting Information for:

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

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General considerations.

Poly[3-mercaptopropylmethylsiloxane] (PMMS, SMS-992, M.W. 4000~7000, 95 cst) was purchased from Gelest Inc. Triallyl cyanurate (TAC), 2,2-Dimethoxy-2-phenylacetophenone (DMPA), hexadecyltrimethylammonium bromide (CTAB) were purchased from Aladdin (Shanghai) Inc. Dichloromethane, triethylamine and DMF were distilled from CaH₂ under argon. THF was distilled from sodium-benzophenone ketyl under argon. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere. All flash chromatography were performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

All ¹H NMR spectra were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) and recorded in CDCl₃ (internal reference 7.26 ppm). A Sigma 2K 15 centrifuge was used for isolation of the polymers after precipitation. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 °C/min from -10 °C to 130 °C.

A UV lamp ($20 \text{ mW}\cdot\text{cm}^{-2}$, $\lambda = 365 \text{ nm}$; LP-40A; LUYOR Corporation) was used to irradiate the samples to perform the photo-crosslinking reactions. All NIR-responsive experiments were performed using a 808 nm semiconductor laser source (Output power: 5W, Center wavelength: $808 \pm 3 \text{ nm}$, Nanjing Latron Laser Company, China).

Polarized optical microscopy (POM) observations of the liquid crystalline textures of the monomers, polymers and elastomers were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with a Phenix Phmias2008 Cs Ver2.2 software. UV spectra were obtained with a TU-1810 ultraviolet-visible spectrophotometer (UV/VIS spectrometer) (Beijing Purkinje General Corp., China). The solution temperature variation measurements were performed using an ETS-D5 contact thermometer (IKA Corp., Germany).

All gold concentrations were measured by ICP-OES technique (Optima 5300DV inductively coupled plasma optical emission spectrometer, PE Corp., America). The morphological analyses of GNRs in either aqueous or organic solution were all performed by a JEM-2100 transmission electron microscope (JEOL-TEM, Japan). The morphological analyses of GNR/LCE composite fibers were performed by an Inspect F50 field emission scanning electron microscope (FEI-SEM, America).

GNR/LCE composite fiber samples were sliced by an Ultramicrotome (Powertome XI, RMC, Inc. America). The obtained sliced pieces were immediately examined by a JEM-1400 transmission electron microscope (JEOL, Japan).

1H), 7.03 (d, J = 8.5 Hz, 4H), 4.21 (s, 2H), 4.10 (d, J = 4.6 Hz, 4H), 2.65 – 2.29 (m, 4H), 1.86 (d, J = 6.5 Hz, 4H), 1.73 – 1.41 (m, 14H), 1.05 (t, J = 7.3 Hz, 6H), 0.76 – 0.51 (m, 2H), 0.11 (s, 3H).

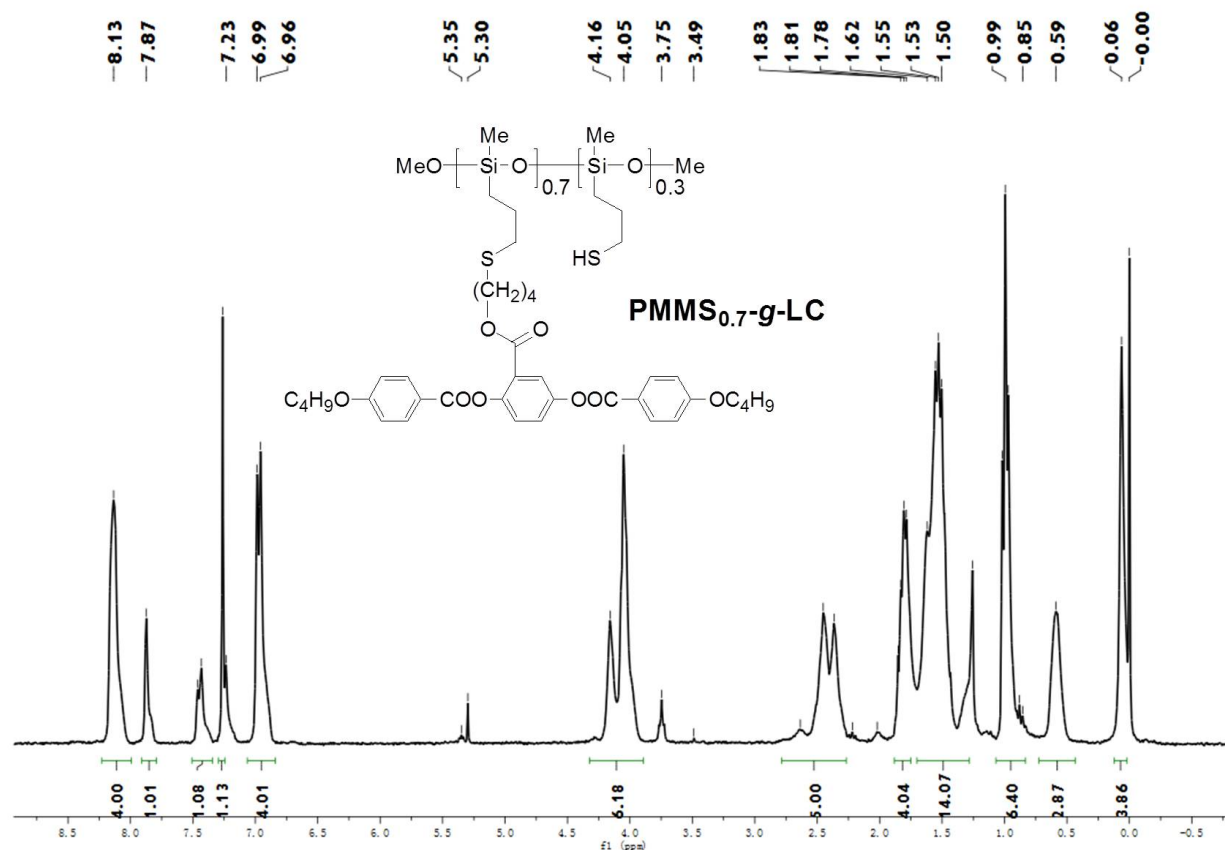


Fig S2. NMR spectrum of partially functionalized LCP $\text{PMMS}_{0.70}\text{-g-LC}$.

The mesomorphic property of PMMS_{0.70}-g-LC

Under POM observation, PMMS_{0.70}-g-LC shows following phase transition: Nematic- 51 °C - Isotropic (on heating), Isotropic - 50 °C - Nematic (on cooling).

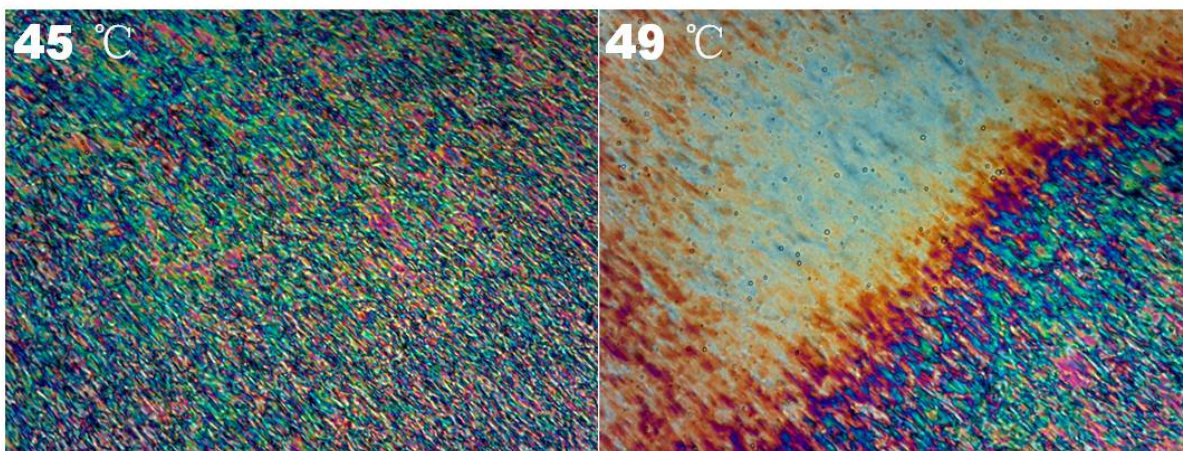


Fig S3. POM images of partially functionalized LCP PMMS_{0.70}-g-LC.

Preparation of **o**horgano-soluble GNRs

(1) **Synthesize of water-soluble GNRs in aqueous solution.** Au nanorods were fabricated by a one-pot synthesis using phenol reduction according to literature report.^[2] To prepare the growth solution, 3.0 mL of H₂AuCl₄ (conc. 0.01 M), 0.8 mL of silver nitrate (conc. 0.02 M), and 4×10⁻⁴ mol of hydroquinone were sequentially added into 71.25 mL of CTAB (conc. 0.11 M) solution under slight shaking, followed by standing for 5 min. Then, 0.26 mL of NaBH₄ (conc. 0.498 mM) solution was added and kept standing for over 12 h. All experiments were conducted inside a 30 °C incubator.

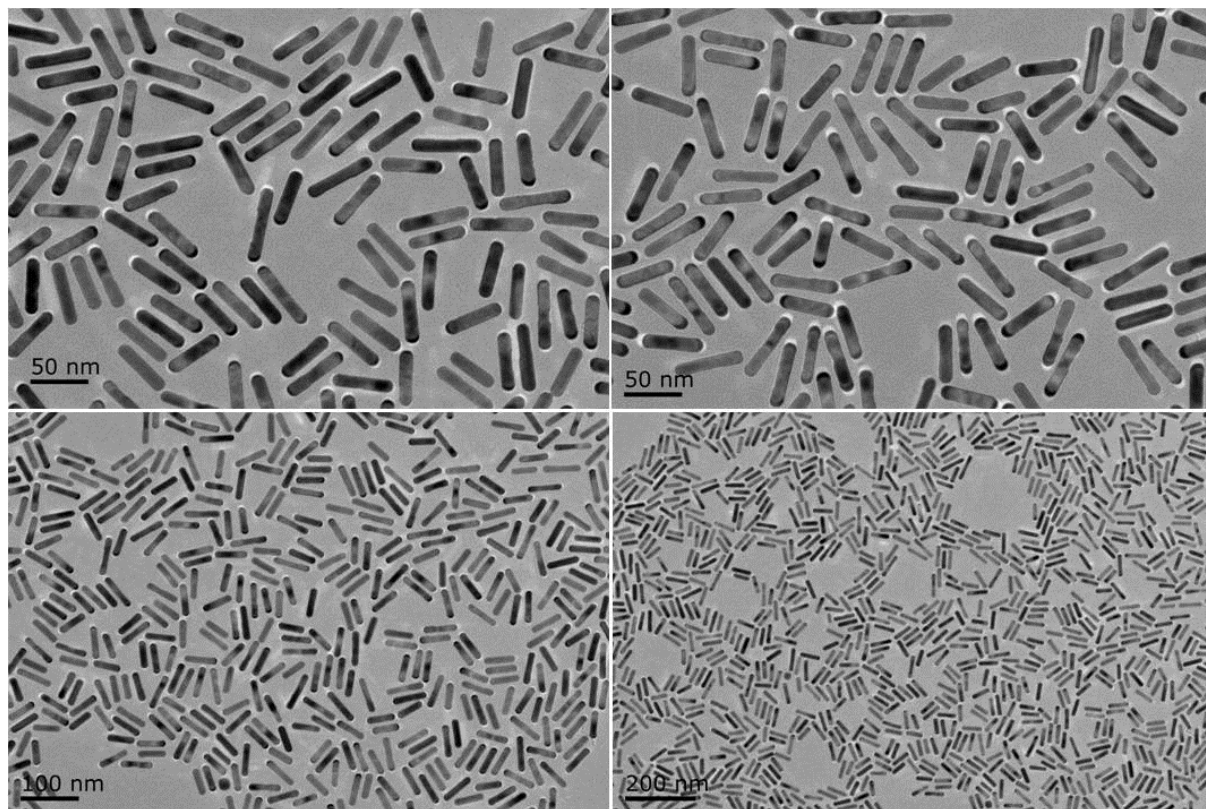


Fig S4. TEM images of GNRs produced in aqueous solution.

(2) **Surface functionalization of GNRs with PMMS by ligand exchange to prepare ~~oil-~~solubleorgano-soluble GNRs.** As shown in Fig S4S5-S6, firstly, 8 mL aqueous GNR solution was centrifuged and redispersed in 2 mL water. Then, 2.5 mL toluene containing 50 mg PMMS was added into the above 2 mL aqueous GNR solution. After that, 4 mL acetone was slowly added and the mixture was stirred vigorously at 28 °C for about 5 mins. The upper red layer was collected and then centrifuged under 15000 r/min for 15 mins. The supernatant was discarded, the resulting precipitate was redispersed in THF. The above centrifuge-redisperse procedure was repeated for three times and the final solution was concentrated to 1 mL, containing the desired GNRs which were steadily dispersed in THF.

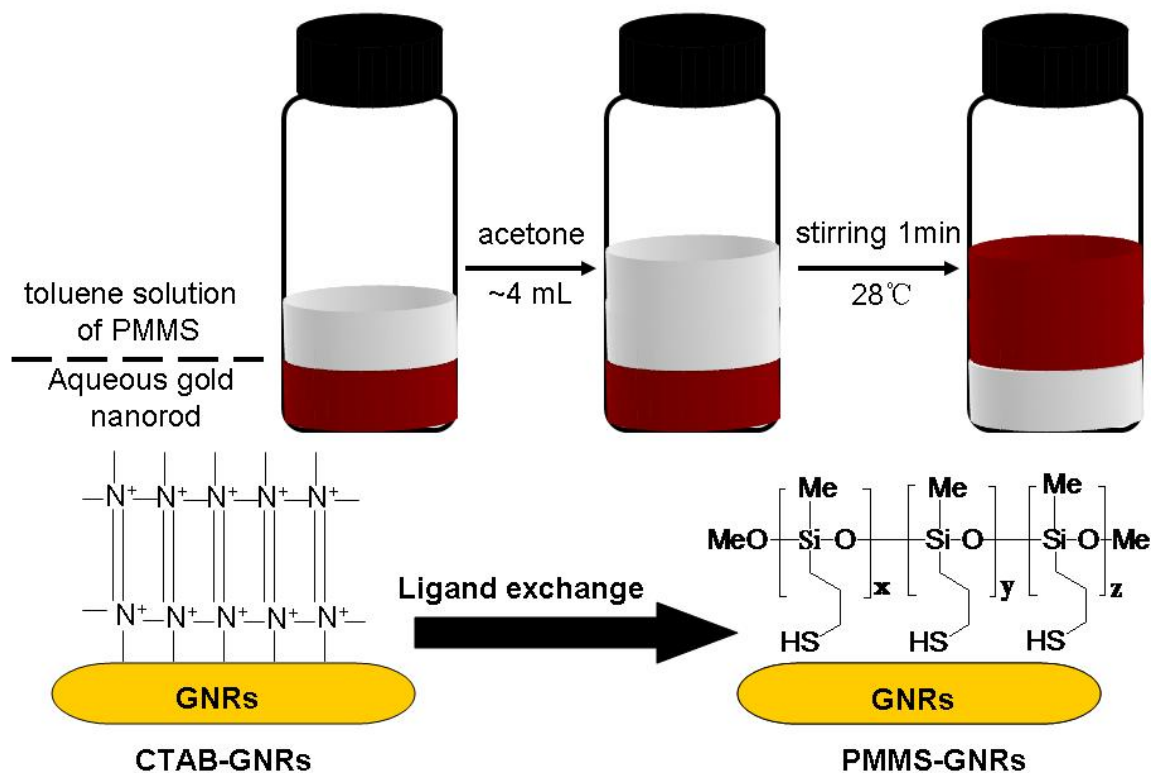


Fig S5. Schematic illustration of the principle of preparing oil-soluble organo-soluble GNRs.

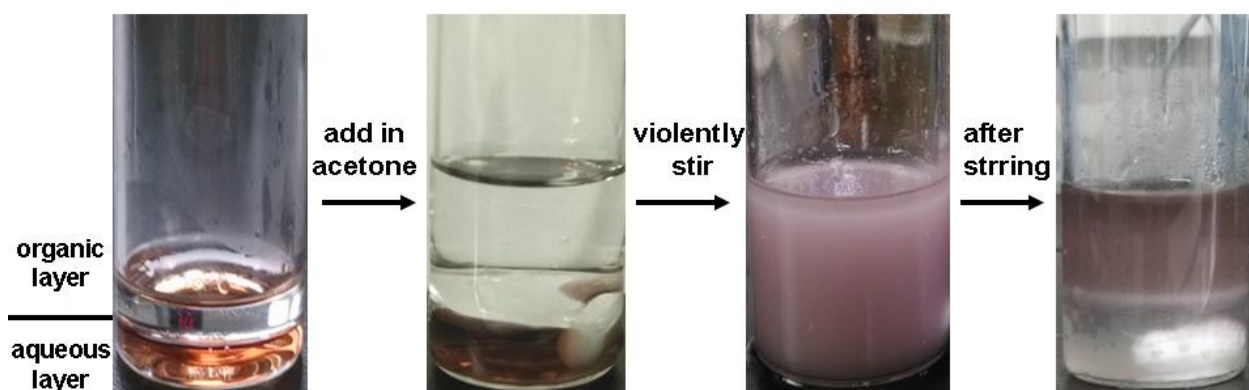


Fig S6. Experimental photos of the process of preparing organo-soluble GNRs.

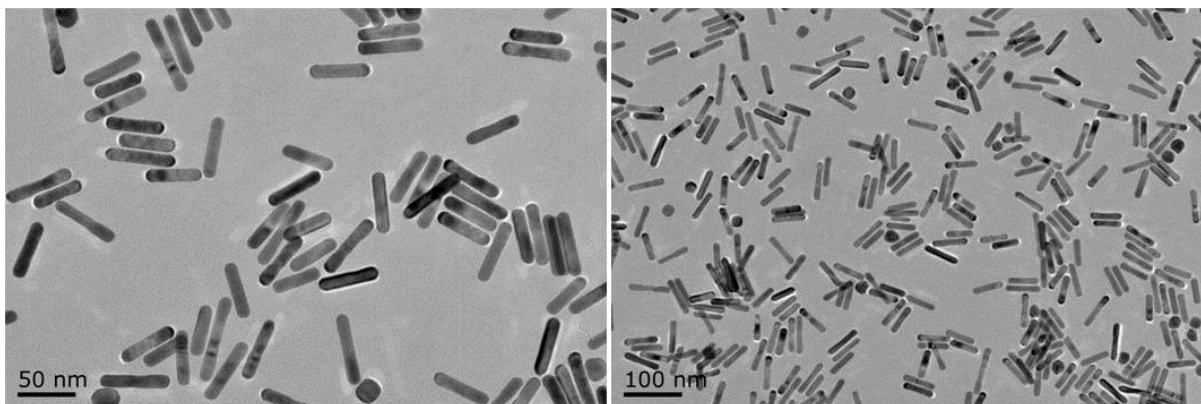


Fig S6S7. TEM images of GNRs stabilized by PMMS in THF solution.

Explanantion for the fact that a blue-shift in the signal of longitudinal surface plasmon resonances of GNRs after ligand-exchange

When the dimension of metal nanoparticles, such as gold, silver, is small enough compared to the wavelength of incident light, the surface plasmon can be excited due to the collective oscillations of the conduction band electrons.^[2] This optical properties induced by Surface Plasmon Resonance (SPR) greatly depend on particle size, shape, and even the local environment. As far as GNR is concerned, this phenomenon is more obvious.^[3] For example, many literatures have pointed out that the absorption wavelength of the maximum in the longitudinal plasmon band is linearly proportional to the aspect ratio of Au rod.^[4] Meanwhile, if there is aggregation scenario occurring for GNR, the oscillating electrons in one Au rod will feel the electric field due to the oscillation of the free electrons in a second Au rod, which can lead to a collective plasmon oscillation of the aggregated system and the further occurrence of blue-shift of absorption band.^[5] In our work, such limited GNR aggregation mainly occurred during the ligand exchange between CTAB and PMMS on the surface of Au nanorod. It should be pointed out that the slight blue-shift of absorption band of GNR occurring in the ligand-exchange process have been reported.^[6] All the above explains the fact that a blue-shift in the signal of longitudinal

surface plasmon resonances of GNRs was observed after exchanging the CTAB with PMMS ligand.

Preparation of GNR/LCE composite fibers

PMMS_{0.70}-g-LC (210 mg, 0.12 mmol free -SH), TAC (cross-linker, 15.0 mg, 0.06 mmol), DMPA (photoinitiator, 3.07 mg, 0.012 mmol) were added into a 5 mL vial. The mixture was fully dissolved in 1 mL dry THF, and then mixed well with the prepared 1 mL GNR/THF solution. The organic solvent was then removed in *vacuo*. The vial was placed on a hot stage and heated to 50 °C. When the mixture became viscous, the fibers were drawn by dipping the tip of a capillary pipet and pulling the mixture with it as quickly as possible. The fibers were then placed on a microscope slide which has been surface-treated with several drops of silicone oil to prevent fibers to stick on the glass. At r.t., the fibers were irradiated by using a UV-lamp for 30 minutes.

Preparation of pure LCE fibers

PMMS_{0.70}-g-LC (330 mg, 0.20 mmol free -SH), TAC (cross-linker, 24.9 mg, 0.10 mmol), DMPA (photoinitiator, 5.12 mg, 0.02 mmol) were added into a 5 mL vial. The mixture was fully dissolved in 1 mL dry THF, the organic solvent was then removed in *vacuo*. The vial was placed on a hot stage and heated to 50 °C. When the mixture became viscous, the fibers were drawn by dipping the tip of a capillary pipet and pulling the mixture with it as quickly as possible. The fibers were then placed on a microscope slide which has been surface-treated with several drops of silicone oil to prevent fibers to stick on the glass. At r.t., the fibers were irradiated by using a UV-lamp for 30 minutes.

ICP-OES measurement method of determining Au wt% of GNR/LCE composite fibers

GNR/LCE composite fiber sample (14 mg) was fully dissolved in 1.0 mL aqua regia for 2 days. The solution was then diluted in ultrapure water to achieve 25.0 mL volume. The diluted solution was analyzed as 5.02×10^{-4} mg Au per milliliter by ICP-OES technique. Thus, the gold weight percentage of GNR/LCE composite fiber was determined as 0.09 wt%.

Microtome experiments of GNR/LCE composite fibers (0.09 Au wt%)

GNR/LCE composite fibers were embedded in a highly crosslinked acrylate and methacrylate based polymer media, using a modification of the typical method used for preparation of biological samples for electron microscopy. To make the 1–2 cm long fibers parallel to the surface of slicing mold, fibers were placed between two very thin plastic plates. Space between the plates was fully filled with Lowicryl-HM20 resin. The two plastic plates were put in a $-75\text{ }^{\circ}\text{C}$ dry-ice/acetone bath and the HM20 resin was photopolymerized by irradiation with long wavelength (365 nm) ultraviolet light for 2 days. This way, GNR/LCE composite fibers were embedded in the polyacrylate resin matrix, which was then cut into small pieces containing the fibers. A small block of embedded fiber was glued to the top surface of an iron mold, which was then held in an Ultramicrotome. The slice thickness was set to 65 nm per cut, and the obtained sliced pieces were immediately examined by TEM.

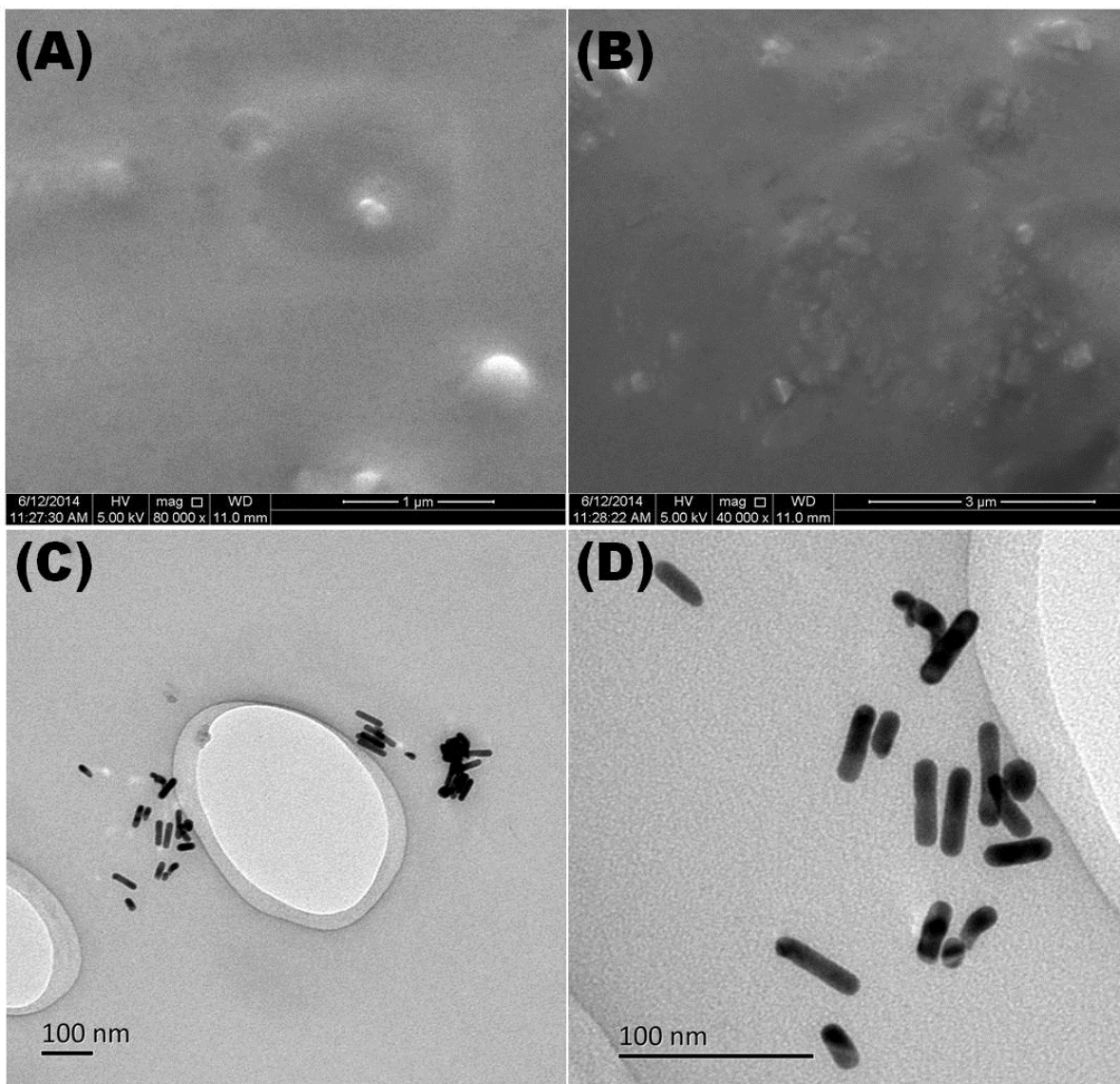


Fig [S7S8](#). (A, B) SEM images of GNR/LCE composite fiber's surface. (C, D) TEM images of longitudinal sections (65 nm thick) of GNR/LCE composite fiber ([0.09 Au wt%](#)) sliced by an ultramicrotome.

Preparation of GNR/LCE composite fibers with a higher Au loading-level

Firstly, 40 mL aqueous GNR solution was centrifuged and redispersed in 2 mL water. Then, 2.5 mL toluene containing 50 mg PMMS was added into the above 2 mL aqueous GNR solution. After that, 4 mL acetone was slowly added and the mixture was stirred vigorously at 28 °C for about 5 mins. The upper red layer was collected and then centrifuged under 15000 r/min for 15 mins. The supernatant was discarded, the resulting precipitate was redispersed in THF. The above centrifuge-redisperse procedure was repeated for three times and the final solution was concentrated to 1 mL, containing the desired GNRs which were steadily dispersed in THF.

PMMS_{0.70}-g-LC (210 mg, 0.12 mmol free -SH), TAC (cross-linker, 15.0 mg, 0.06 mmol), DMPA (photoinitiator, 3.07 mg, 0.012 mmol) were added into a 5 mL vial. The mixture was fully dissolved in 1 mL dry THF, and then mixed well with the above prepared 1 mL GNR/THF solution. The organic solvent was then removed in *vacuo*. The vial was placed on a hot stage and heated to 50 °C. When the mixture became viscous, the fibers were drawn by dipping the tip of a capillary pipet and pulling the mixture with it as quickly as possible. The fibers were then placed on a microscope slide which has been surface-treated with several drops of silicone oil to prevent fibers to stick on the glass. At r.t., the fibers were irradiated by using a UV-lamp for 30 minutes.

The gold weight percentage of this GNR/LCE composite fiber was determined as 0.47 wt% by ICP-OES technique described above.

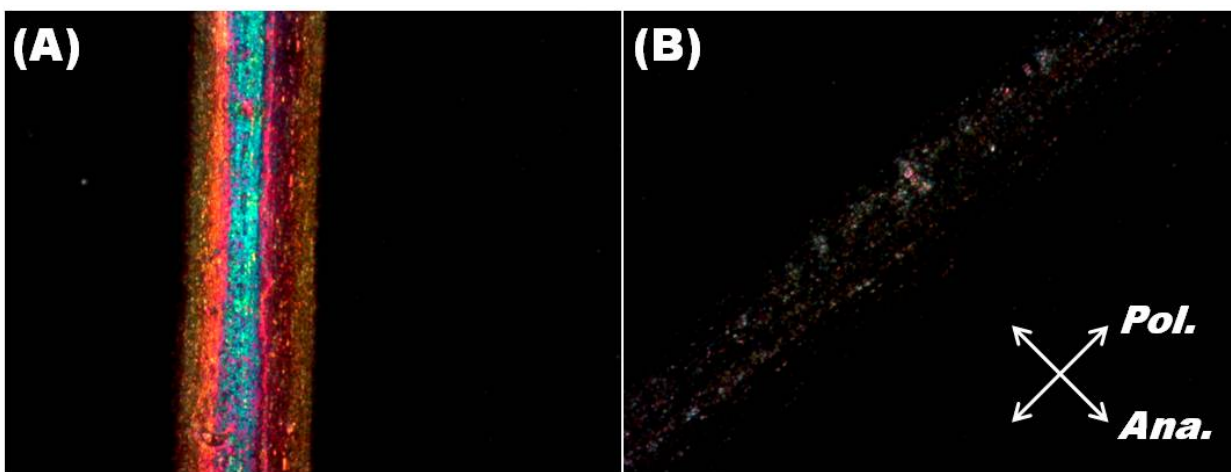


Fig S9. POM images of GNR/LCE composite fiber sample (0.47 Au wt%) oriented at the angle either (A) 45° or (B) 0° to the polarizer.

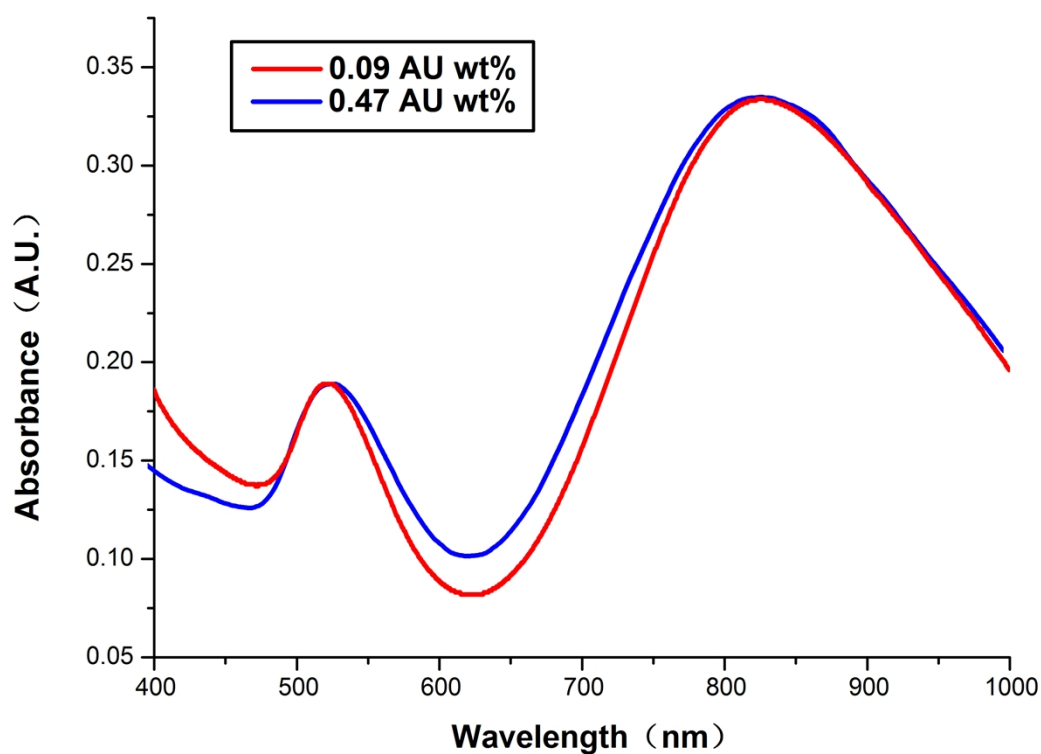


Fig S10. UV-Vis spectra of GNR/LCE composite samples with 0.09 wt% and 0.47 wt% Au-loadings respectively.

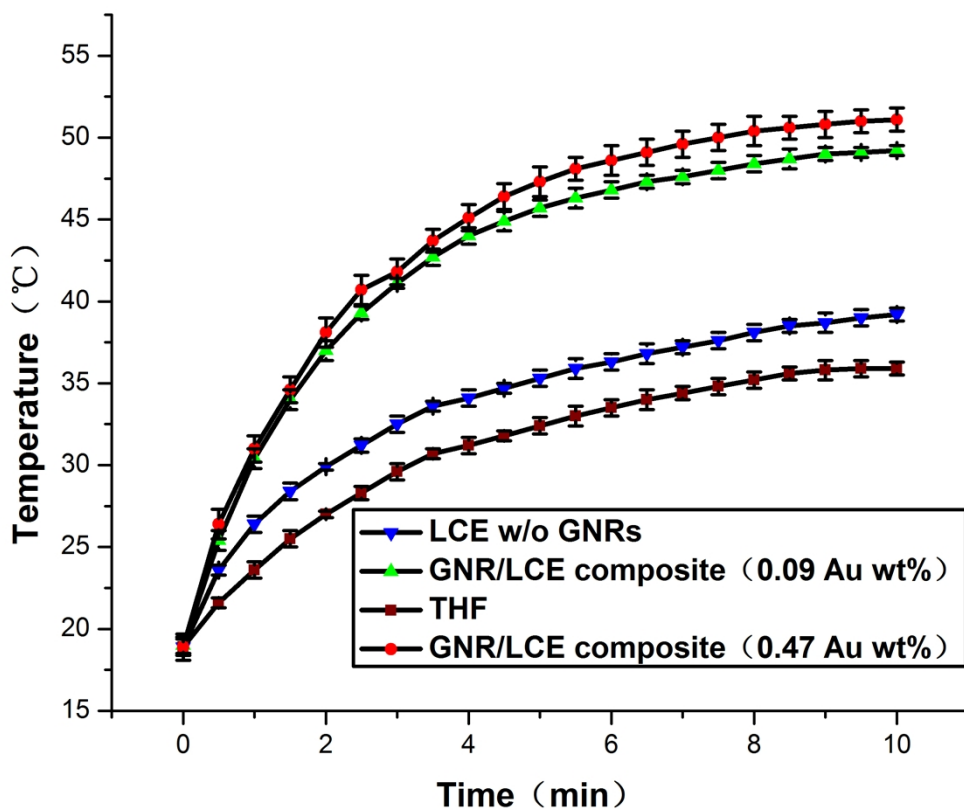


Fig S11. A diagram of temperatures of THF reference solutions containing none, pure LCE fiber, two GNR/LCE composite fibers with 0.09 wt% and 0.47 wt% Au-loadings respectively vs. NIR illumination time.

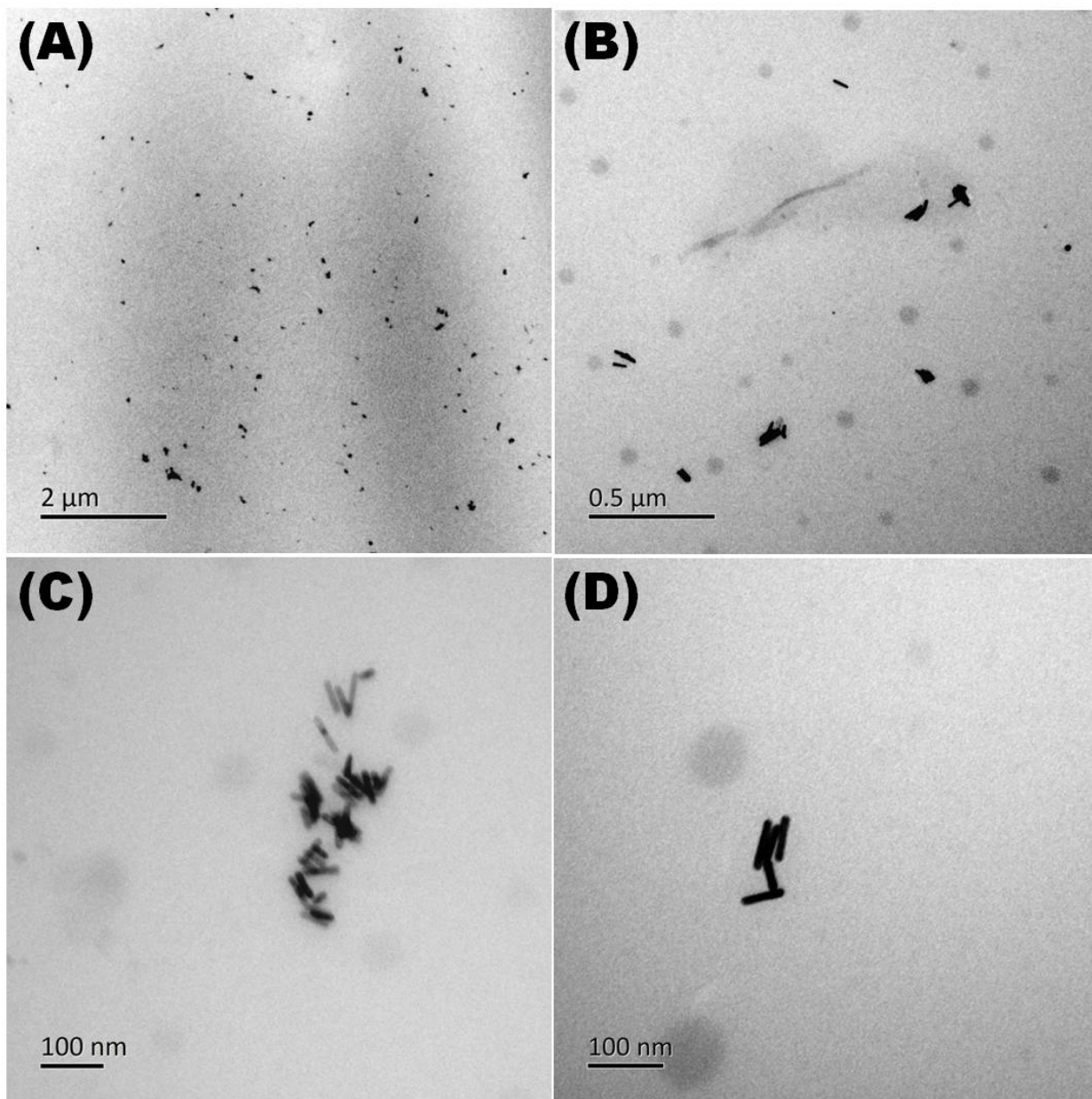


Fig S12. TEM images of longitudinal sections (100 nm thick) of GNR/LCE composite fiber (0.47 Au wt%) sliced by an ultramicrotome.

Reference

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