Journal of Materials Chemistry A

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Supporting Information

Bio-inspired Stimuli-responsive Graphene Oxide Fibers from Microfluidics

Luoran Shang,[a, b] Yuetong Wang,[a] Yunru Yu,[a] Jie Wang,[a] Ze Zhao,[a] Hua Xu,[a] and Yuanjin Zhao[a*]

a. State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China.

b. School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States

METHODS

Materials. Sodium alginate (low viscosity) and calcium chloride (anhydrous) were derived from Alfa Aesar. N-Isopropylacrylamide (NIPAM, 97%), N, N-Methylenebis(acrylamide), the photo-initiator 2-hydroxy-2-methylpropiophenone (HMPP), and the hydrophobic reagent octadecyltrichlorosilane (OTS) were all purchased from Sigma-Aldrich. Fluorescent polystyrene nanoparticles (F8811 (excitation/emission: 505/515 nm) were purchased from Invitrogen. Graphene oxide (GO) suspension was purchased from XF NANO, Inc. Ethanol and n-hexadecane was gained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Water with a resistivity of 18.2 MΩ•cm-1 was acquired from a Millipore Milli-Q system. All other chemical reagents were of the best grade available and used as received.

Microfluidic chip construction. The capillary microfluidic devices consisted of coaxial assemblies of round (World Precision Instruments, Inc) and square (AIT Glass) glass capillaries on glass slides. The first and second inner capillaries were tapered using a laboratory portable Bunsen burner (Honest MicroTorch) to reach an orifice diameter of about 50 and 100 μm. The middle capillary was tapered by a micropipette

puller (Sutter Instrument Co., Novato, USA) and was sanded under optical microscope to reach the desired orifice diameter of 200-300μm. The outer capillary has an outer diameter of 1 mm and an inner diameter of 580 μm. The inner wall of the outer capillary was wetted by the hydrophobic reagent octadecyltrichlorosilane (OTS) and soon incubated for 30 min for hydrophobic treatment. After this, the solution was blown out by nitrogen. Then the three capillaries were coaxially assembled in a square capillary with an inner diameter of 1.05 mm. A transparent epoxy resin (Devcon 5 Minute Epoxy) was used to seal the tubes where required.

Fibers generation. The first phase I_1 was pre-gel aqueous solution of sodium alginate (2 wt%). The second inner phase I_2 was aqueous solution of calcium chloride (2 wt%). The middle phase M was aqueous mixture of GO (2 mg/ml) suspension and NIPAM precursor (10wt%) with 1vol% HMPP as photoinitiator. The outer phase O was n-hexadecane. Each fluid was pumped by a syringe pump (Harvard PHD 2000 Series), and was connected through a polyethylene tube (Scientific Commodities Inc., with inner and outer diameters of 0.86 mm and 1.32 mm, respectively.) with a glass syringe (SGE Analytical Science). The I_1, I_2, and M phases flowed through the first inner capillary, the second inner capillary, and the middle capillary, respectively, in the same direction. The continuous phase O flowed *via* the interstices between the square capillary and the middle capillary, or between the square capillary and the outer capillary. A typical set of the flow rates of the I_1, I_2, M, and O phases were 0.1mL/h, 0.1 mL/hm 1.5mL/h, and 10mL/h. The droplets in the fibers were solidified downstream upon *in situ* UV irradiation for 3s by a UV-light (EXFO OmniCure SERIES 1000, 365nm, 100W). The generated GO fibers were collected a container with n-hexadecane and then transferred into a water tank after photo-polymerization. Then, the fibers were washed by ethanol and deionized water for many times before characterization.

Characterization. The microfluidic generation process in the collection capillary of the device was observed in real time under an inverted microscope (AE2000, Motic) The process was recorded by a charged coupled device (CCD, S-PRI F1, AOS Technologies AG). The optical images of the microfibers

were obtained through a stereomicroscope (NOVEL NTB-3A, Ningbo Yongxin Optics Co., Ltd, China) and were captured by a CCD (Media Cybernetics Evolution MP 5.0 RTV). Fluorescence photographs of the microfibers were taken by a Laser Scanning Confocal Microscope (Carl Zeiss, LSM510). The microstructures of microfibers were characterized by a scanning electron microscope (SEM, HITACHI, S-3000N). Raman spectroscopy was conducted using a Raman platform (RAMAN, inVia, Renishaw) with a 532-nm laser. XRD pattern was obtained through an X-ray diffractometer (D8 FOCUS, Bruker). FTIR spectrum was measured using a FTIR spectroscopy system (ThermoFisher Scientific).

Fog-capture behavior. The GO fibers were hung on a self-prepared holder and were placed in a humid environment (with humidity 60-80%), which was generated by an airbrush kit (OPHIR ART). The microfibers with water droplets captured on the spindle-knots were imaged and recorded by the same stereomicroscope and CCD as before.

NIR-responsive behavior. The photothermally responsive phase transition of the GO/NIPAM composite hydrogel was first investigated. By using a mask with a designed pattern, a butterfly-shaped hydrogel membrane was fabricated after UV-induced polymerization of the GO/NIPAM mixture solution. The membrane was then exposed to laser irradiation for 1-3 min at a distance of 3-5 cm. The source of irradiation was a diode laser (FC-808-4000-MM, SFOLT Co. Ltd) equipped with an optic fiber. After the shrinkage, the laser was switched off to let the membrane swell again under natural state. The photothermally responsive behaviors was repeated several times and observed under the same stereomicroscope and CCD as before. For the investigation of the water collection performances of the fibers, the water-hung GO fibers were exposed to the same laser irradiation and observed in the same way before.

SUPPORTING FIGURES

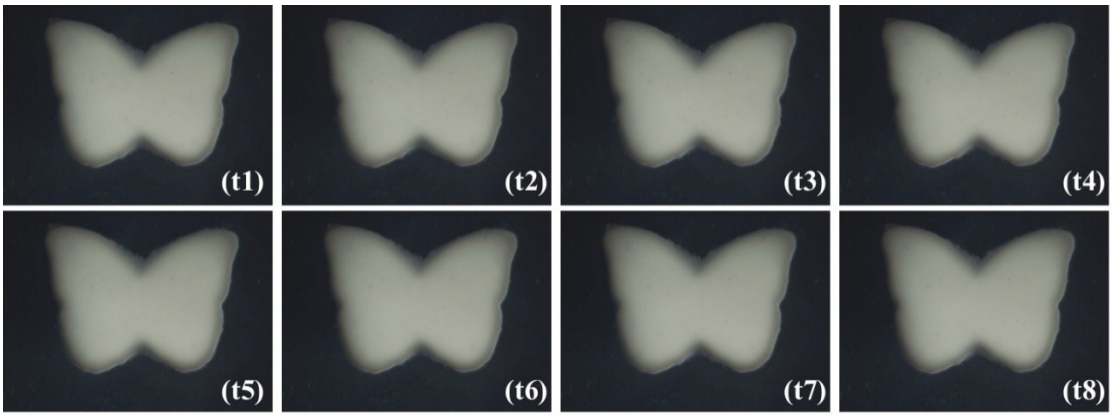

Figure S1. The pure NIPAM hydrogel under NIR irradiation: (t1-t5) with laser switched on; (t6-t8) with laser switched off.

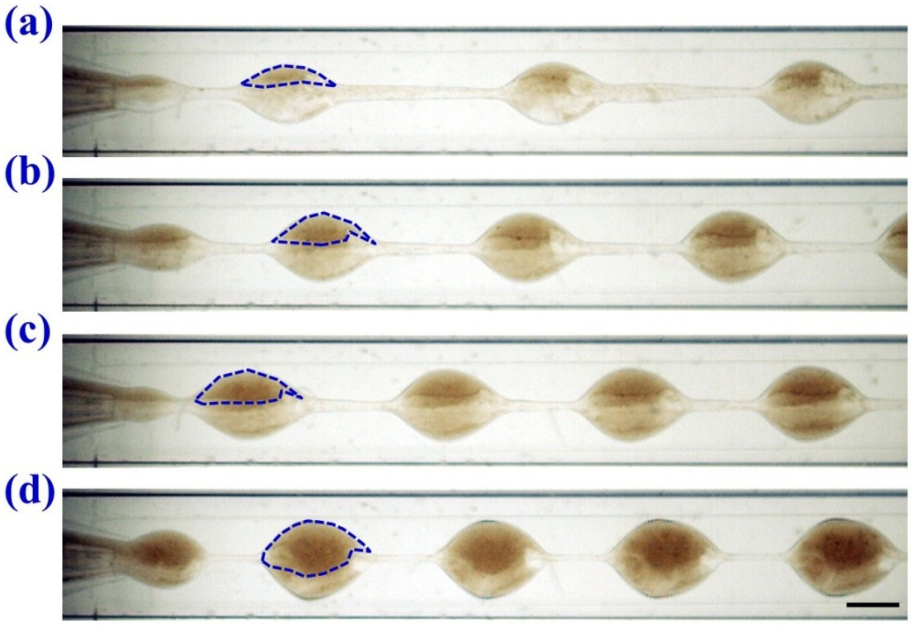

Figure S2. Microfluidic spinning and emulsification when F_1 and F_2 were too high. In these cases, the emulsification was disturbed, resulting in a nonuniform GO distribution, as marked by the blue dotted areas.

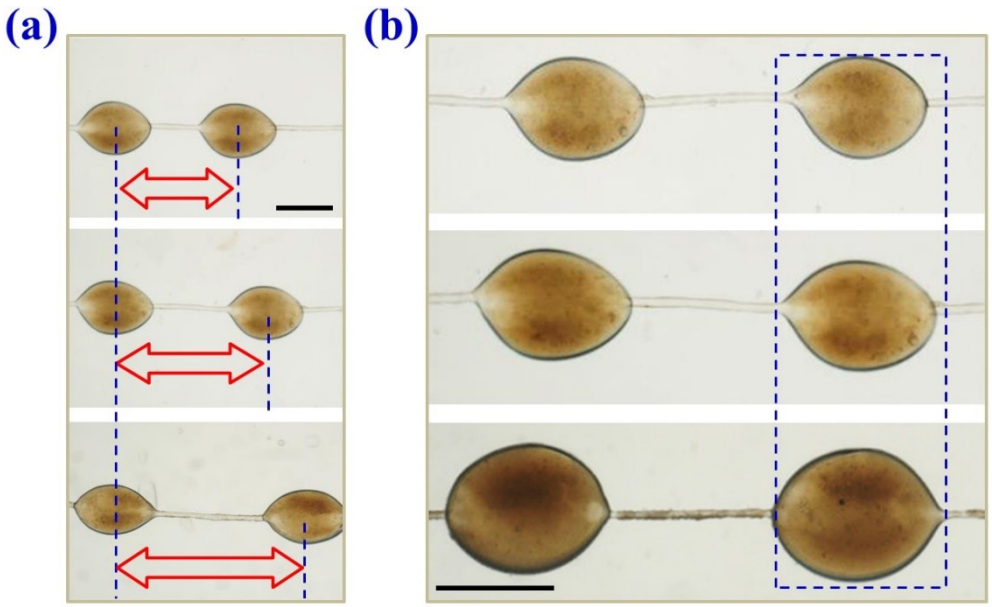

Figure S3. The resultant fibers with (a) different distances between the spindle knots and (b) different sizes of the spindle knots. The scale bar represents 400 μm.

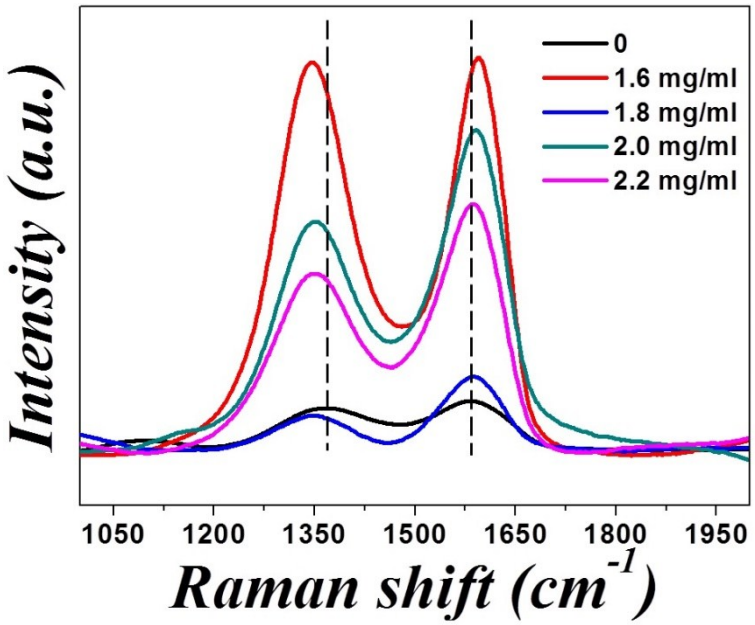

Figure S4. Raman spectra of the spindle knots prepared with different concentration of GO. The black dotted lines depict the peak positions. Compared with pure GO, the G peak of the GO/NIPAM composite spindle knots was blue-shifted from 1590 cm^{-1} to 1602 cm^{-1}, and D peak was red-shifted from 1365 cm^{-1} to 1350 cm^{-1}.

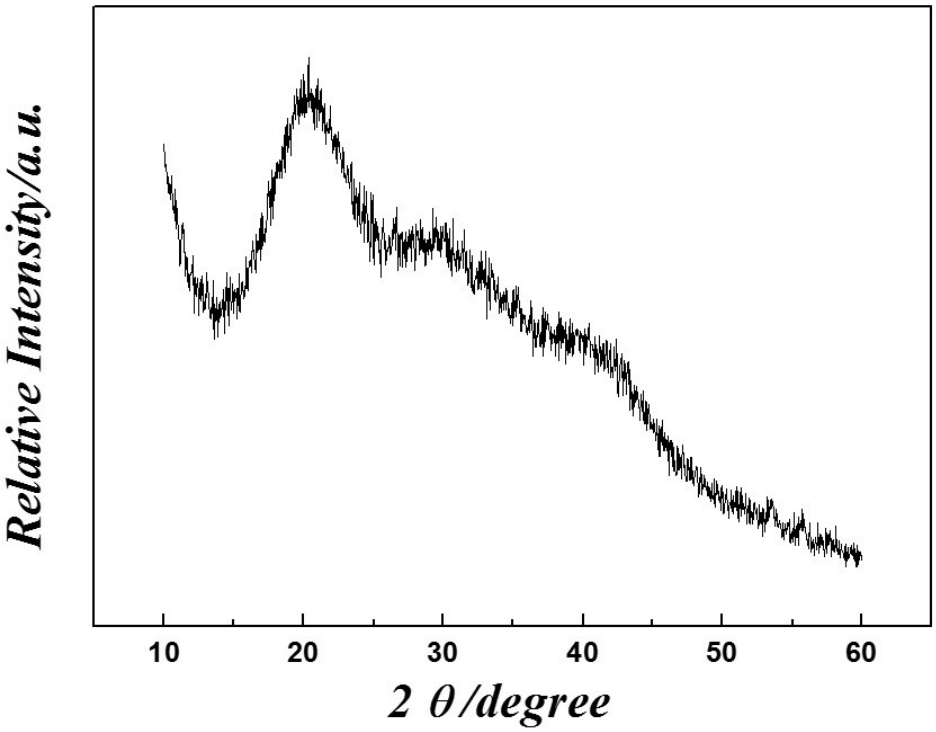

Figure S5. XRD pattern of spindle knots composed of GO/NIPAM composites. It showed diffraction peak of PNIPAM with diffraction peak at $2\theta=20.36^{o}$ while no typical diffraction peak of GO, which indicated that the GO sheets were dispersed well into the polymer matrix.

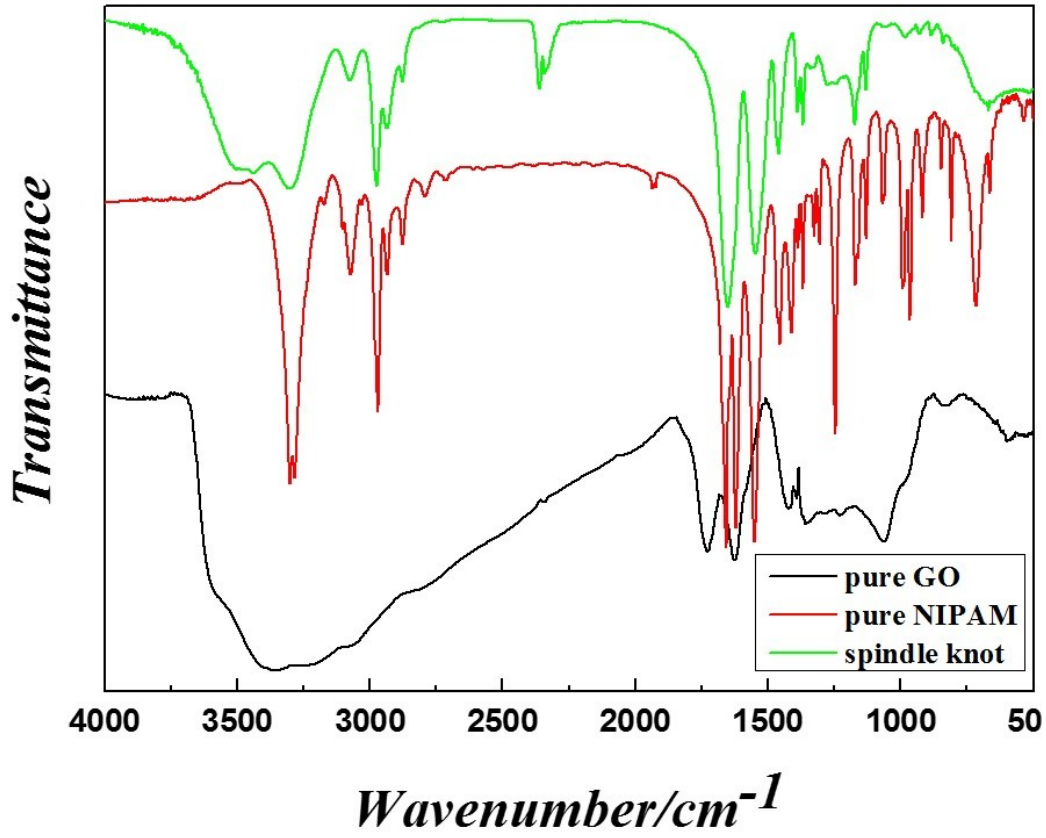

Figure S6. FTIR spectrum of pure GO, NIPAM, and spindle-knots composed of GO/NIPAM composites. In the spectrum of GO, a broad band at 3378 cm^{-1} is attributed to the -O-H group; the bands at 1728 cm^{-1} and 1624 cm^{-1} are attributed to carbonyl species. In the spectrum of GO/NIPAM spindle-knots, the bands at 3378 cm^{-1}, 1728 cm^{-1} and 1624 cm^{-1} disappeared, whereas bands at 2974 cm^{-1}, 1651 cm^{-1} and 1544 cm^{-1} appeared, attributing to the -C-H, –C=O, and -N-H groups, respectively, which are also shown in the spectrum of NIPAM. These results suggested that, in the composite spindle knots, GO is considered to be cross-linking agent.

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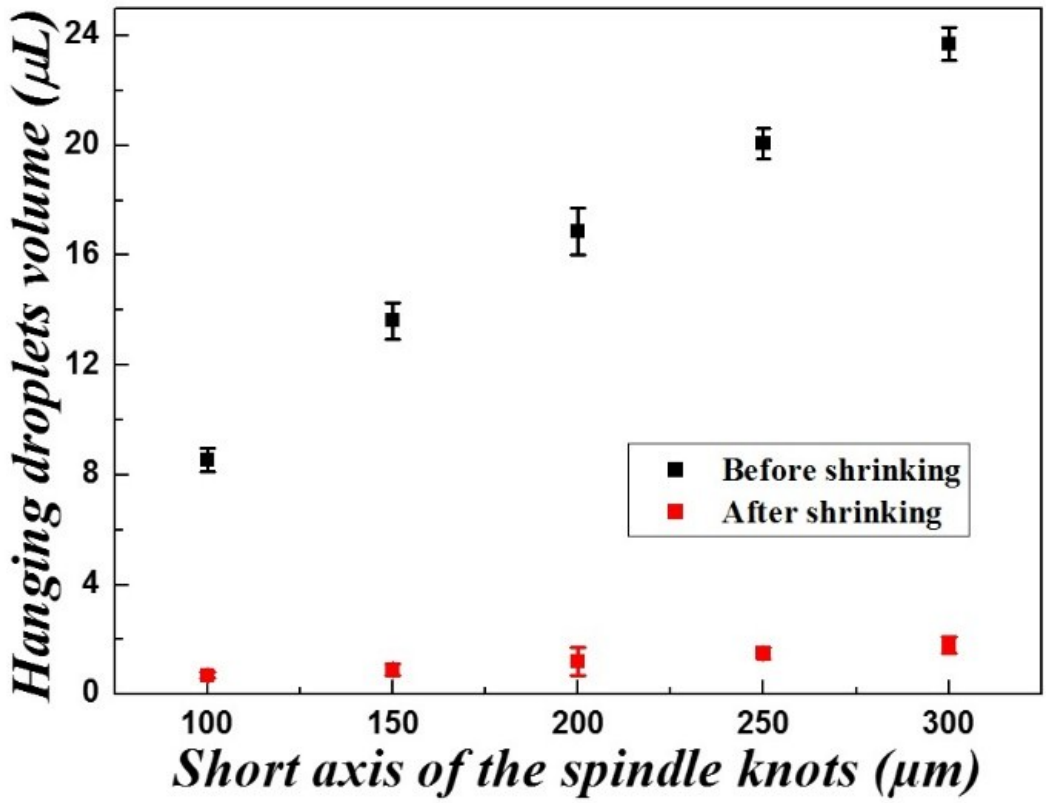

Figure S7. Volume of hanging droplets before and after shrinkage of the spindle knots. The long axis of the spindle knots was 500 μm and the distance between the spindle knots was 1000 μm.