

Supplementary Information for

A one-step strategy for thermal- and pH- responsive graphene oxide interpenetrating polymer hydrogel networks

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1. Experimental Section

1.1. Materials. Expandable graphite powders were kindly provided by Yingtai Co. (China). *N*-isopropylacrylamide (NIPAM) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and recrystallized from cyclohexane before use. Acrylic acid (AA) was purchased from aladdin reagent Co. and purified by passing through a short alumina column. Potassium persulfate (KPS) was purchased from Sinopharm Chemical Reagent Co. Ltd. and recrystallized from water before use. Sodium dodecyl sulfate (SDS), epichlorohydrin (ECH), *N, N'*-methylenebisacrylamide (MBAA) were all purchased from aladdin reagent Co. and used as received.

1.2. Instruments and Measurements. Atomic force microscopic (AFM) images were obtained using a Multimode Nano 4 in the tapping mode. For AFM observations, the samples were dispersed in appropriate solvents (0.2 mg/mL) with the aid of sonication and then spin-coated onto freshly cleaved mica surfaces. SEM images were recorded on a TS 5136MM scanning electron microscope. The dried samples were ground to fine powder and were placed on the copper conductive tape. The temperature-dependent average hydrodynamic radius and its distribution of the PNIPAM-co-AA particles in dilute dispersions were measured on a laser diffraction particle size analyzer (Malvern) in a quartz cell (1x1 cm). The diffraction wavelength of PNIPAM microgel concentrated dispersion was determined on a Hitachi U-2910 UV/Vis spectrophotometer at 20 °C in a quartz cell (1x0.1 cm). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 470 spectrometer. All FTIR samples were prepared as pellets using spectroscopic grade KBr. Raman spectra and image were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 633 nm laser

excitation. The samples were placed onto a clear glass plate. X-ray diffraction (XRD) patterns were acquired by a D8 ADVANCE and DAVINCI.DESIGN (Bruker) X'pert diffractometer with Cu K α radiation. The dried samples were ground to fine powder and flattened on the silicon plate. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 20 °C/min. Calorimetric measurements were performed on a Mettler-Toledo differential scanning calorimeter thermal analyzer at a scanning rate of 10 °C/min from 3 to 70 °C. The wet samples were sealed into an alumina crucible.

2. Preparation Procedure

2.1. Preparation of GO Sheets. GO sheets were synthesized by a modified Hummers method. Expandable graphite powders (5 g), potassium permanganate (15 g) and concentrated H₂SO₄ (115 mL) were mixed together. After keeping in the ice bath for 2 h, the reaction mixture was heated to 35 °C and stirred continuously for 0.5 h. 115 mL distilled water was slowly added to the reaction vessel, stirred for another 15 min and further diluted with 700 mL warm distilled water (40 °C) before adding 50 mL 30% H₂O₂. The resulted suspension was filtered, washed with 5% HCl and dialyzed for 7 days in the dark. Subsequently, the wet form of GO was freeze-dried before use.

2.2. Preparation of PNIPAM-co-AA Microgels. Monodisperse PNIPAM-co-AA microgels were prepared by precipitation polymerization. NIPAM monomer (3.8 g), AA monomer (0.27g), *N, N'*-methylenebisacrylamide (0.066 g) and sodium docecyl sulfate (0.15 g) were dissolved in deionized water (240 mL). The solution was heated to 70 °C and bubbled with nitrogen for 1 h, then potassium persulfate (0.166 g) dissolved in 5 mL deionized water was added to initiate the reaction. The polymerization proceeded for 4 h under stirring at 300 rpm. The resultant microgel dispersions were dialyzed for 5 days and concentrated to 3.7 wt% before use.

2.3. Preparation of GO/PNIPAM IPN Hydrogel and PNIPAM Microgel Network. GO/PNIPAM IPN hydrogel was synthesized as follows. 2 mL PNIPAM-co-AA microgel aqueous solution (3.7wt%) and 2 mL GO aqueous dispersion (0.2wt%) were mixed in a reaction tube. 2mL ECH was then slowly injected into the bottom of the reaction tube. The reaction tube was sealed and placed at 98 °C for incubation for 24 h. A black soft hydrogel

can be obtained by washing successively by acetone and water. PNIPAM microgel network was synthesized by replacing GO aqueous dispersion by pure water, which resulted to be a brilliant blue gel after sufficient swelling in water at room temperature.

3. Characterization of GO Sheets.

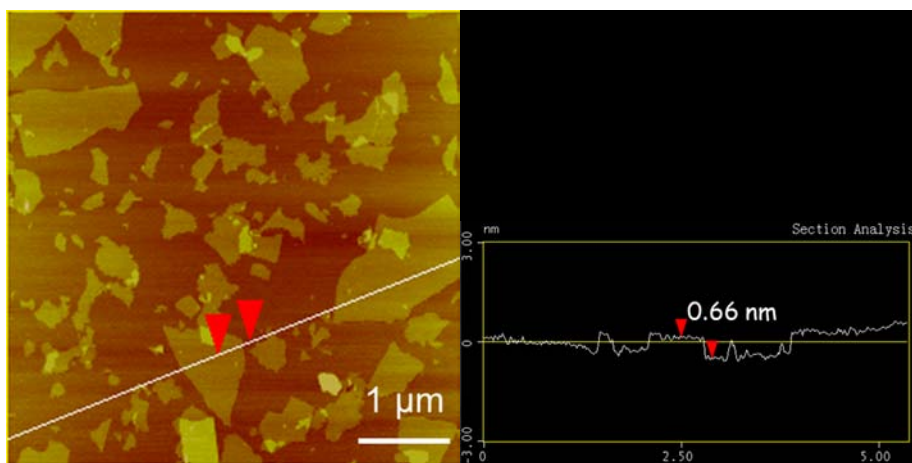


Fig. S1. AFM image of synthesized GO sheets.

4. Characterization of PNIPAM-co-AA Microgels.

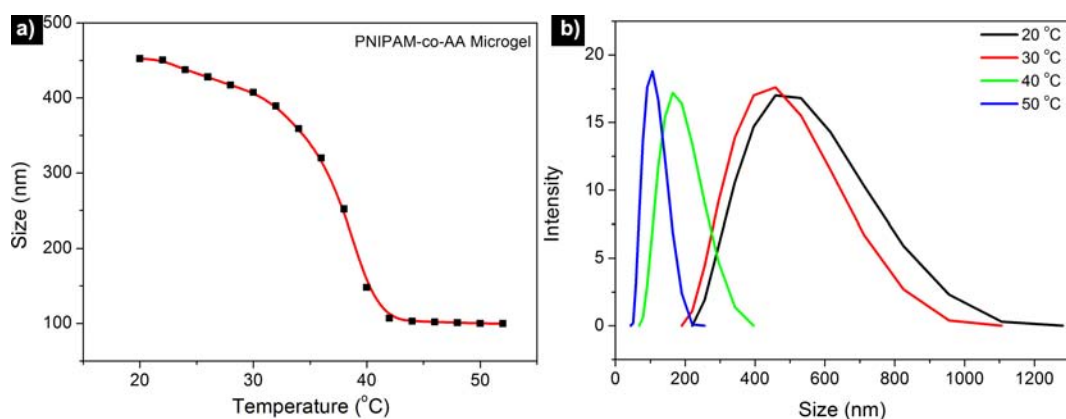


Fig. S2. a) Temperature-dependent average hydrodynamic radius of PNIPAM-co-AA microgel in diluted solution. b) Particle size distribution curve of PNIPAM-co-AA microgel at 20, 30, 40 and 50 °C. Polydispersity (PDI): 20 °C, 0.146; 30 °C, 0.136; 40 °C, 0.186; 50 °C, 0.068.

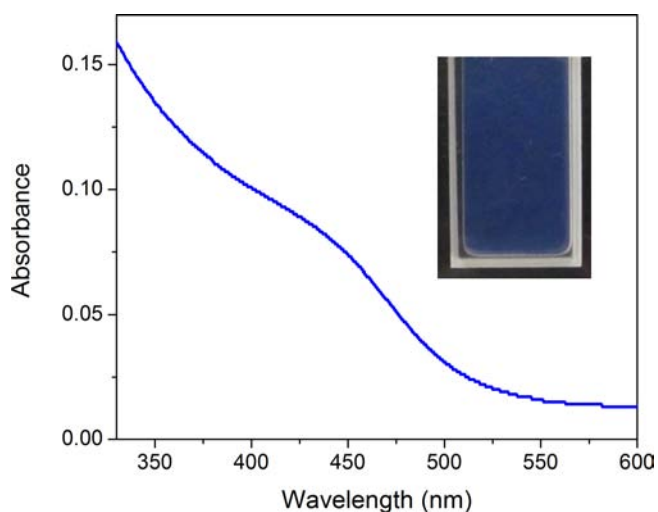


Fig. S3. UV-Vis spectroscopy of 3.7 wt% PNIPAM-co-AA microgel aqueous dispersion at 20 °C. The inset is a photograph of the sample cell (quartz glass).

5. Morphology of Swollen GO/PNIPAM Hydrogel and PNIPAM Microgel Network.

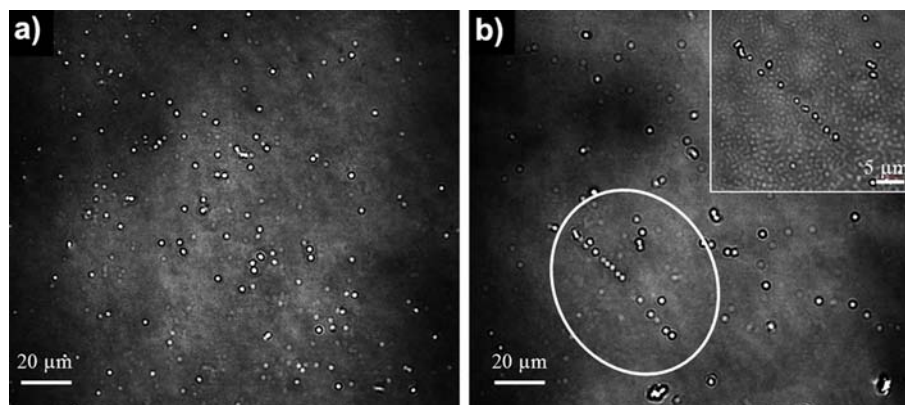


Fig. S4. Laser scanning confocal microscopy images of swollen a) GO/PNIPAM IPN hydrogel and b) PNIPAM microgel network at room temperature (~ 20 °C). The inset figure is the enlarged view of circled region focused on a deeper focal plane.

Wherein, large numbers of nanoparticles can be observed embedded in a cloud-like substrate, which is also close-packing particles from the enlarged view focused on a deeper focal plane. Apparently, the incorporation of GO sheets into PNIPAM microgel network does not affect its inherent two-level structural hierarchy

6. SEM Images of Freeze-Dried Samples.

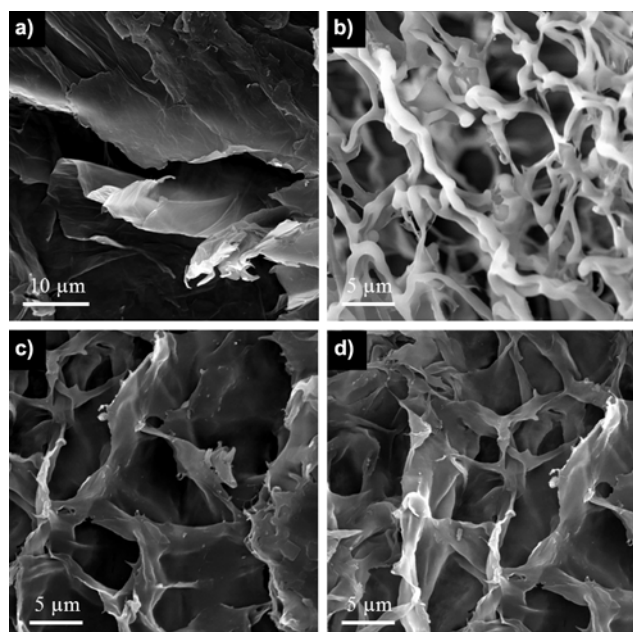


Fig. S5. SEM images of freeze-dried a) GO sheets, b) PNIPAM microgel, c) GO/PNIPAM IPN gel and d) PNIPAM microgel network.

7. Dispersibility of GO Sheets in Swollen GO/PNIPAM IPN Hydrogel.

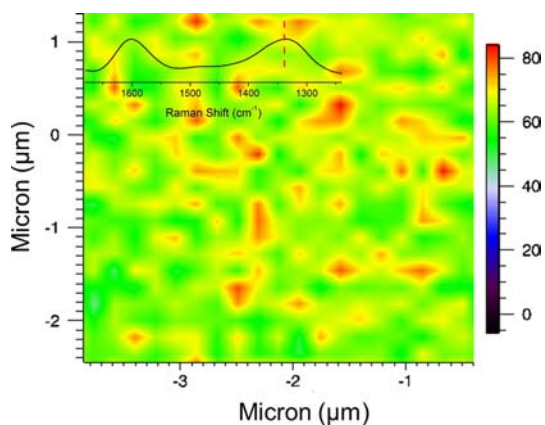


Fig. S6. Confocal Raman image of swollen GO/PNIPAM IPN hydrogel acquired by detecting the intensity of D peak at 1322 cm^{-1} . Wherein, red regions are GO-rich ones, while green regions are where water and PNIPAM microgels are.

8. DSC Curves of GO/PNIPAM Mixture and Linear PNIPAM in Water.

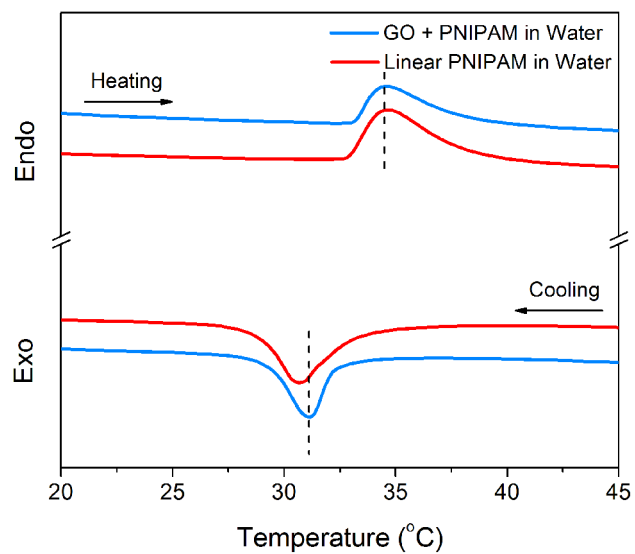


Fig. S7. DSC curves of GO/PNIPAM mixture (0.2/2.5 wt%) and linear PNIPAM (2.5 wt%) in water. Scanning rate: 10 °C/min.