

Electronic Supplementary Information

Thermoresponsive Fluorescence of Graphene-Polymer Composite Based on Local Surface Plasmons Resonance Effect

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Figure S1 presents the fabrication of G-pNIPAM by pNIPAM-amine and G-COOH.

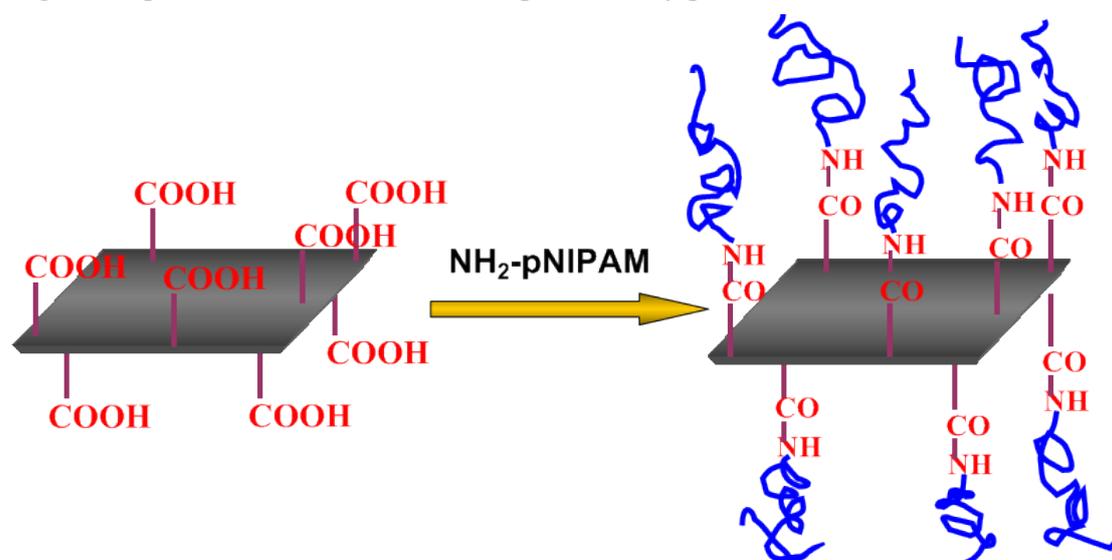


Figure S1. Schematic representation of the fabrication.

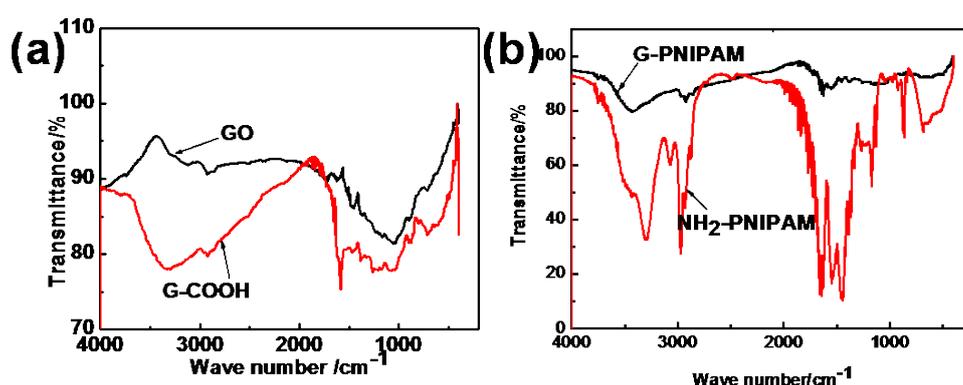


Figure S2. Fourier transform infrared spectra of oxidized graphene (GO), carboxylic graphene (G-COOH) (a) and graphene-PNIPAM composite (G-PNIPAM), NH₂-PNIPAM.

FTIR spectra in Figure S2 verify the synthesis process of G-pNIPAM: obvious

carboxylic groups vibration band²³ at $\sim 3400\text{ cm}^{-1}$ exist in G-COOH (Figure S2a), while after reacting with $\text{NH}_2\text{-pNIPAM}$, vibration of rethane carbonyl²³ at $\sim 1738\text{ cm}^{-1}$ observed (Figure S2b) illustrates the production of G-pNIPAM composite. Also, amide hydrogen²⁴ in $^1\text{H-NMR}$ result (Figure S3) of G-pNIPAM proves the formation of G-pNIPAM composite.

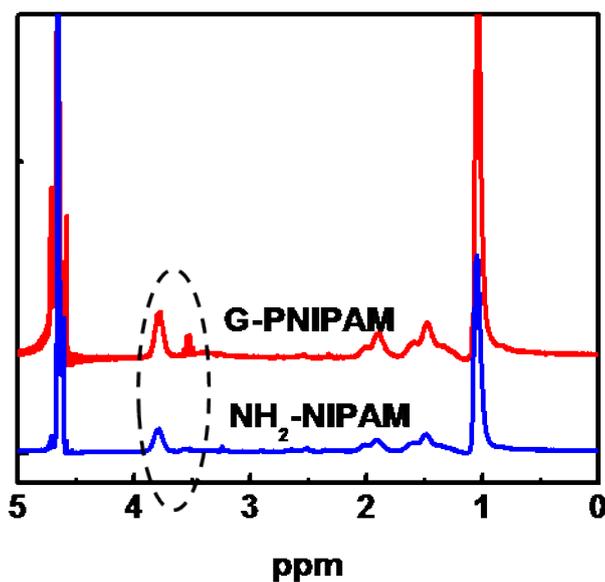


Figure S3. $^1\text{H-NMR}$ spectra for $\text{NH}_2\text{-PNIPAM}$ and G-PNIPAM.

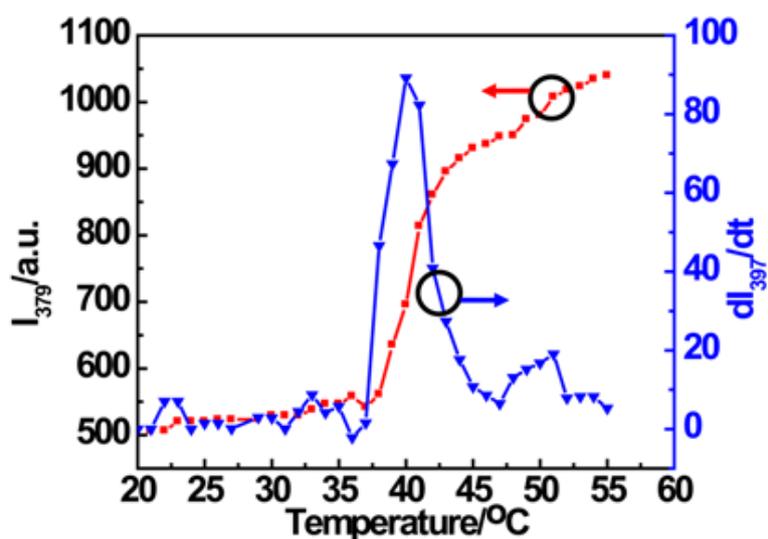


Figure S4. Temperature dependence of ELS intensity (at 379 nm, I_{379}) of Ag@G-PNIPAM solution and the differential curve of I_{379} against temperature.

Laser light scattering (DLS) and elastic light scattering (ELS) of G-pNIPAM solution depending on temperature are showed in Figure S4 to understanding the phase transition of pNIPAM chains on graphene in solution. Dispersed in solution, water molecules around pNIPAM chain would form a highly ordered layer connecting amide groups with hydrogen bonds because of hydrogen bond and Van De Waals force, rendering pNIPAM chains stretched.²⁵ The temperature dependence of ELS intensity of Ag@G-pNIPAM solution in Figure S4b shows that in the early stage of heating from 20 °C to the LCST of pNIPAM (32 °C²⁰), there was no obvious change occurring until it got close to 37 °C and I_{379} began rising sharply. It indicates interaction parameters of pNIPAM chains and water molecules mutating²⁵ and part of the hydrogen bond breakage occurring. The polymer chains began shrinking²⁶ and dehydrating, while inducing the hydrophilic side chains dehydrated,²⁷ which is regared as a signal of initial stage of the phase separation.²⁸ Therefore, the initial stage of phase separation of the polymer chains it is thought to be a little higher than 37 °C, which is just the normal temperature of human body. On the other hand, the maximum change rate of ELS intensity depending on temperature is shown in 39 °C, that is, after grafting with graphene, the LCST of pNIPAM increased to 39 °C from 32 °C²⁰, indicating pNIPAM chains on graphene plates are less mobile than free pNIPAM chains.²⁹ Thus two temperature points (20 °C and 55 °C) at different sides of 39 °C were chosen in our work.

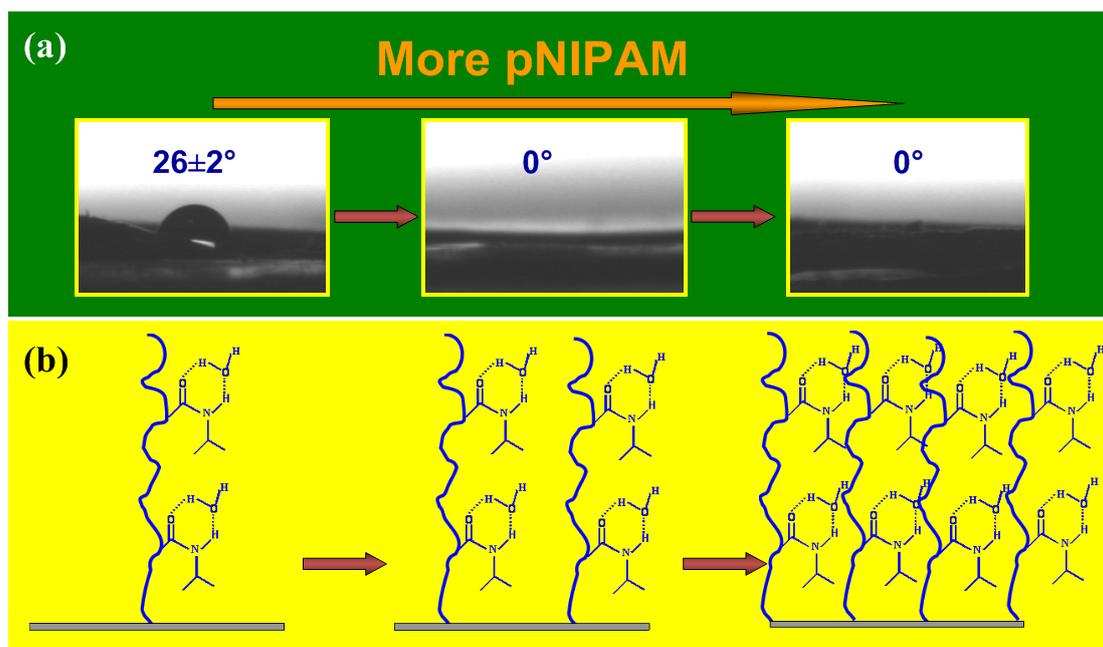


Figure S5. Wettability of flat G-PNIPAM surfaces at 20 °C. (a) Water contact angles(CAs) of $26\pm 2^\circ$, 0° and 0° , respectively when PNIPAM content of G-PNIPAM increasing. (b) Diagram of reversible formation of intermolecular hydrogen bonding between PNIPAM chains and water molecules.

Figure S5 shows the more pNIPAM chains on graphene surface, the more hydrophilic composite surface is, which confirms the molecular mechanism of the thermally response of polymer chains grafted on graphene plates.

Enhancement ratio is calculated by applying Equation (1)³⁵:

$$\text{Enhancement ration} = I_{55}/I_{20} \quad (1)$$

Where I_{55} and I_{20} represent the fluorescence intensity of composite system in 55 °C and 20 °C, respectively.

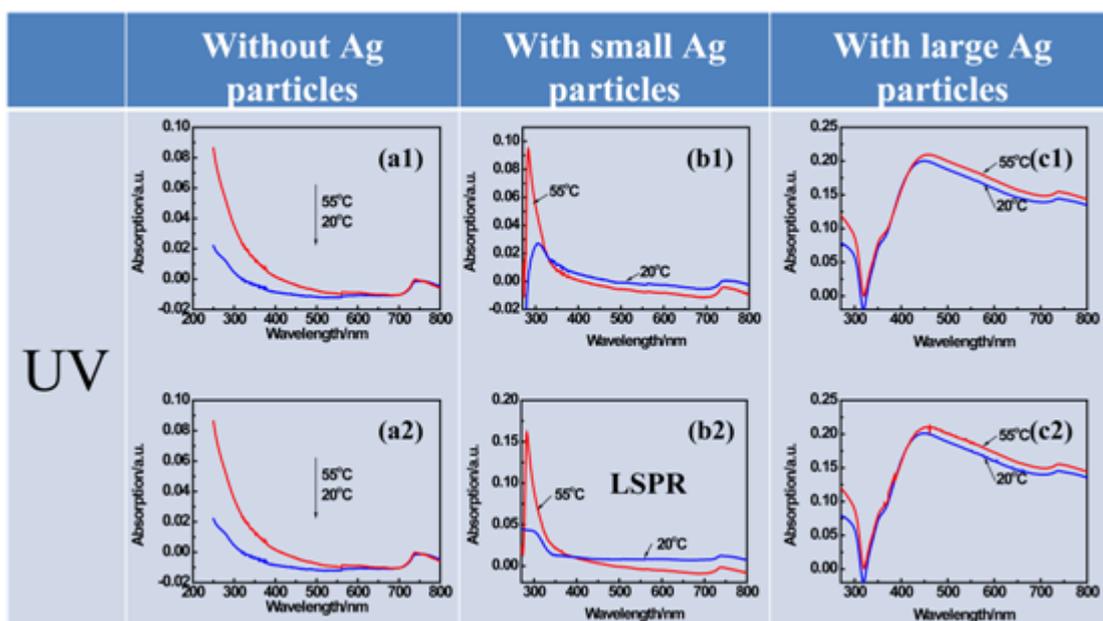


Figure S6. UV-Vis absorption spectra (UV) of the G-PNIPAM without Ag particles (a), G-PNIPAM with small Ag nanoparticles (b) and G-PNIPAM with large Ag nanoparticles (c) in cooling-heating-cooling cycle.

In Figure S6b1, the UV-vis absorption intensity of composite system adding Ag nanoparticles to collapsed microgel dispersion increases a little because of aggregation in 55 °C as that in Figure S6a. However, absorption intensity increases sharply (Figure S6b2) after going through cooling-heating cycle and reaches to 55 °C again when Ag nanoparticles diffuses through polymer network and get to graphene surface. And it decreases again when solution system is cooled to 20 °C again.

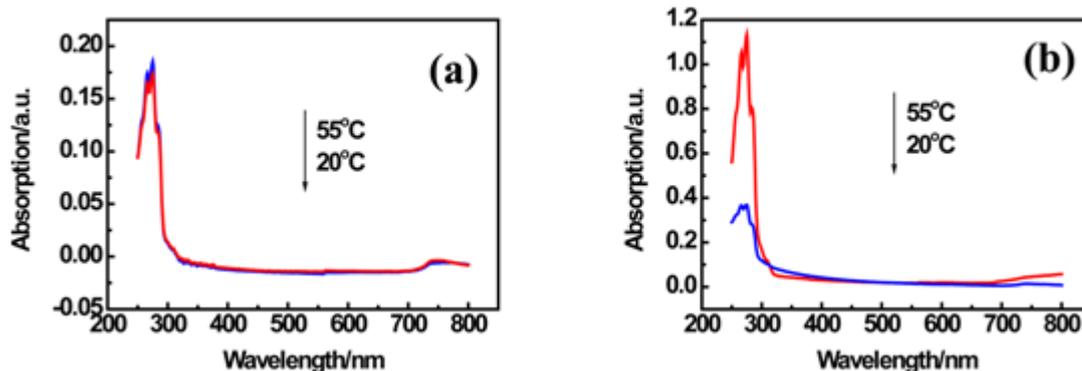


Figure S7. UV-Vis absorption spectra (UV) of the G-PNIPAM with naphthalene nanoparticles in cooling-heating-cooling cycle. (a) nanoparticles never diffuse through the porous polymer shell, (b) nanoparticles interact (55 °C) and non-interact (20 °C) with graphene core.

When fluorescent probe molecule naphthalene are added to collapsed G-pNIPAM microgel dispersion instead of Ag nanoparticles at 55 °C. Undergoing a cooling-heating cycle, naphthalene molecules diffuse through polymer network and are pulled to graphene surface. Absorption intensity increases sharply due to the π - π stacking between graphene and naphthalene (0.4 to 1.3 in Figure S7b). Cooled the solution to below LCST, naphthalene molecules are pushed away from graphene and absorption intensity decreases again (Figure S7b) as the result of Ag@G-pNIPAM dispersion.