Tunable Dual-stimuli Response of a Microgel Composite Consisting of Reduced Graphene Oxide Nanoparticles and Poly(*N*-isopropylacrylamide) Hydrogel Microsphere

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Electronic Supplementary Information (ESI)

S1. Supporting Images

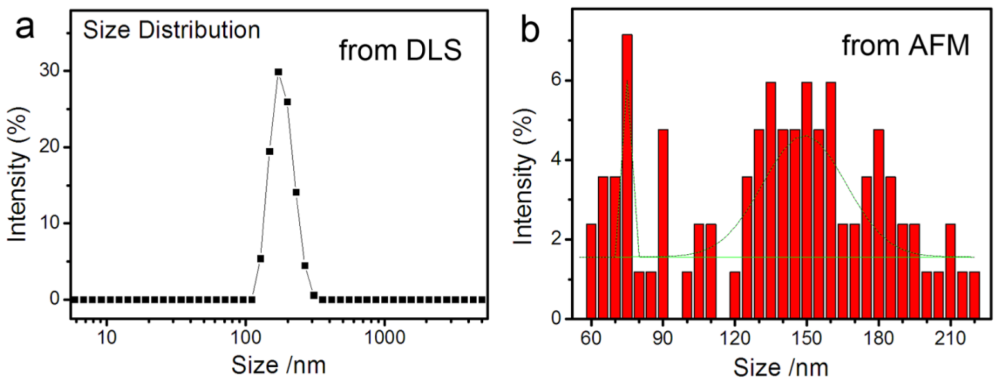
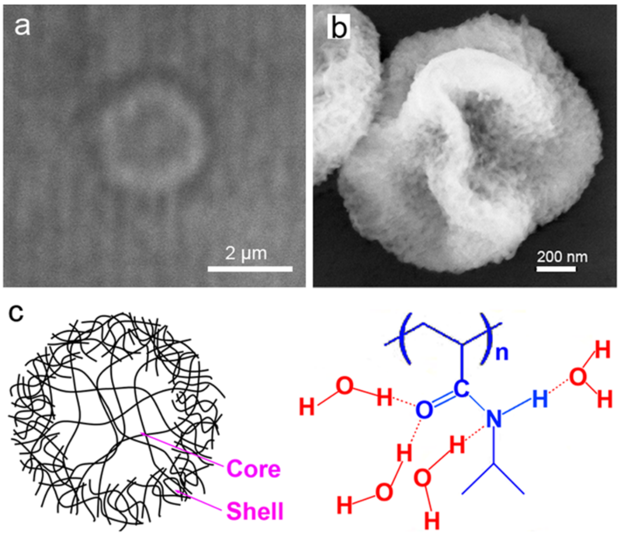


Fig. S1 Size distribution of rGO nanoparticles according to dynamic light scattering (DLS, a) and AFM (b) measurements.



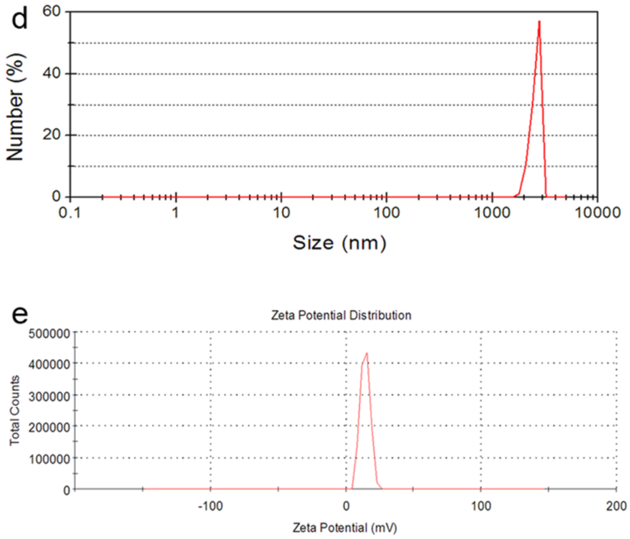


Fig. S2 Optical micrograph (a), SEM image (b), schematic image (c), DLS test (d) and zeta potential profile (e) of the as synthesized pNIPAM microgelspheres. (a), (b) and (c)-left show the core-shell structure of the sphere. (c)-right represents the structure of pNIPAM polymer with hydrated water molecules.

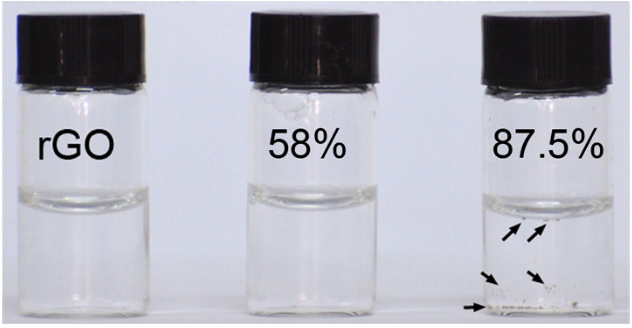


Fig. S3 Digital photograph of composite dispersions with different rGO contents, i.e. 0, 58% and 87.5%, prepared with the same rGO pristine dispersion. Black arrows point out the aggregations.

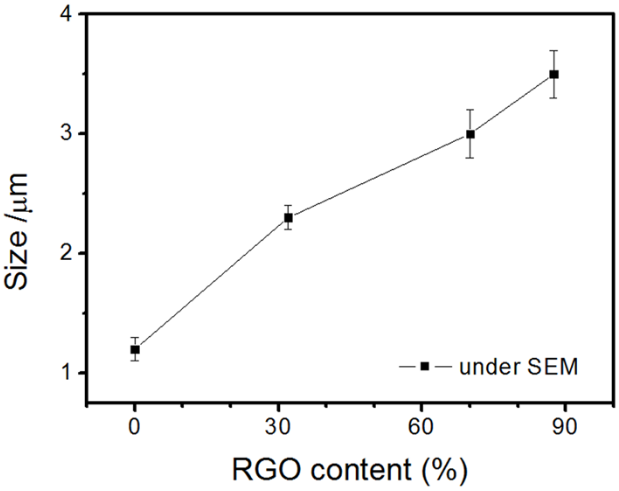


Fig. S4 RGO content dependence of the composite size obtained under SEM observations.

Related Explanation:

The rGO@pNIPAM hydrogel spheres might have fallen in during the freeze drying process for SEM observation. (That is, it might have changed from a sphere to a disk on the platform.) As a result, the size of the composite under SEM is even larger than that under optical microscope.

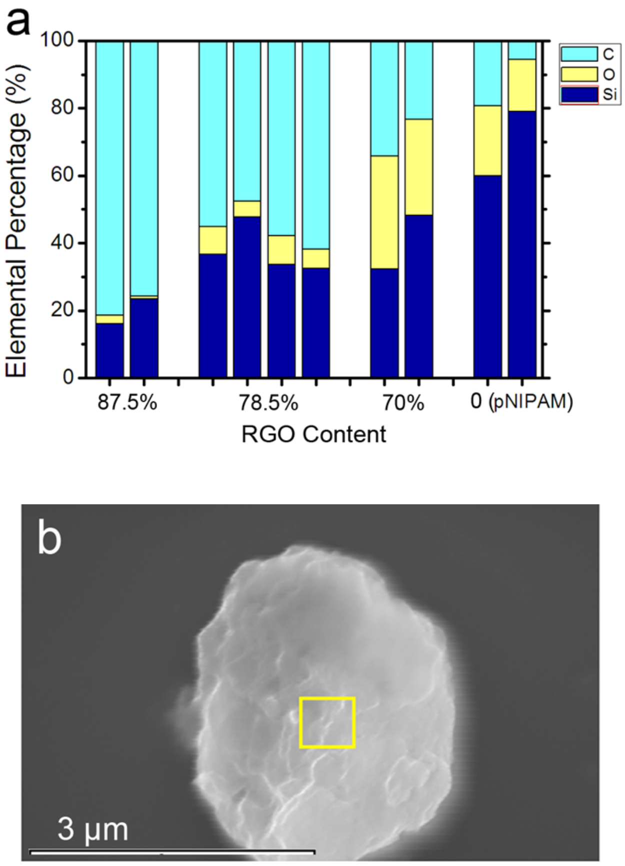


Fig. S5 Elemental analysis of composite with typical rGO contents, i.e. 87.5%, 78.5%, 70%, and the native pNIPAM sphere (freeze-dried on the same silicon substrates). The columns referring to the same type of sample stand for repeated experiments. (b) shows an example of the region selection (marked by the yellow cube) for the elemental analysis under SEM. The white spot is a model freeze-dried 70% rGO sample and the black background refers to the silicon substrate.

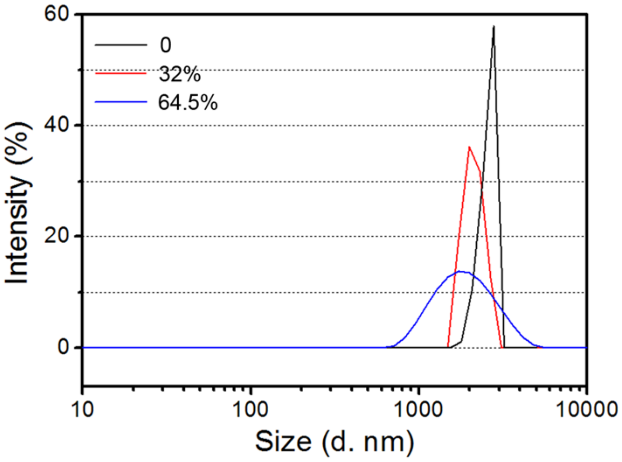


Fig. S6 DLS profiles of composites with 0, 32% or 64.5% rGO content.

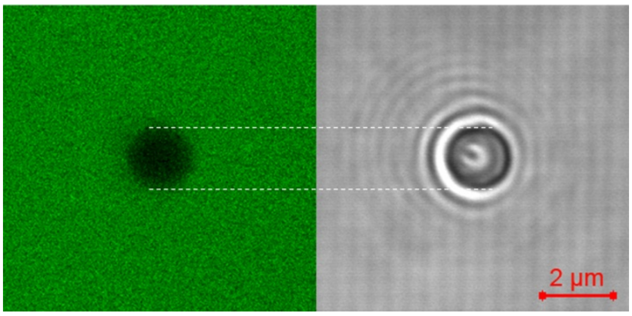


Fig. S7 RGO@pNIPAM composite (~87.5%) takes on as a black sphere under observation, without any calcein infiltration.

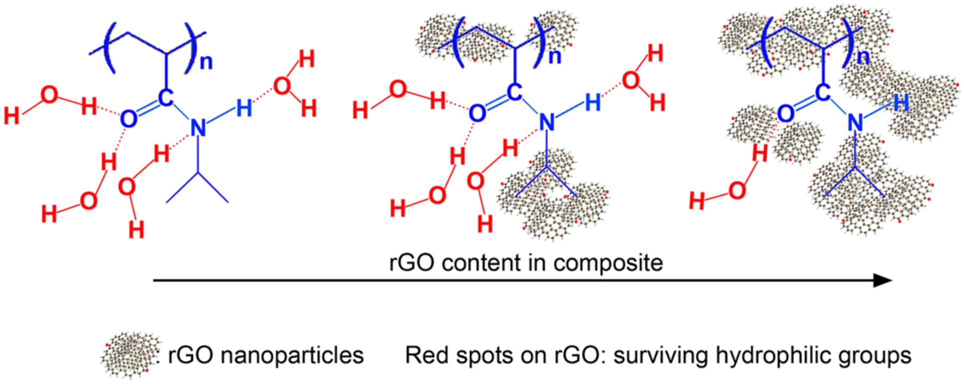


Fig. S8 Schematic images of the structure of pNIPAM polymer with hydrated water molecules and/or adsorbed rGO nanoparticles. With a lower rGO content, the rGO nanoparticles probably adsorbed to the hydrophobic segments of pNIPAM polymer chains; With the increase of rGO concentration, the abundant rGO begins replacing the hydrogen bonded water molecules.

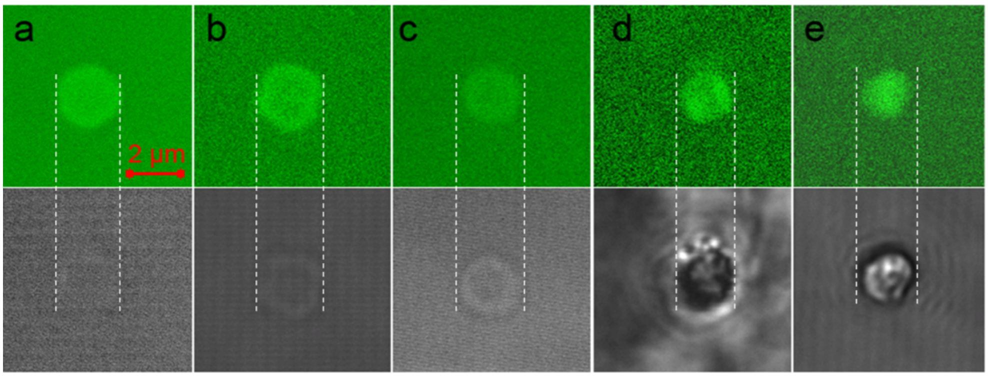


Fig. S9 Comparison of the fluorescence distribution of the calcein loaded composites with different rGO contents: (a) 0, (b) 32%, (c) 47.5%, (d) 64.5% and (e) 78.5%. The bottom row is the transmission image of the corresponding sample.

Related Explanation:

It is observed that from (a) to (c), the fluorescence of the shell region of the composite looks brighter than the core region. In comparison, for (d) and (e), the shell region becomes much dimmer, although it turns to be much more distinguishable in the transmission image.

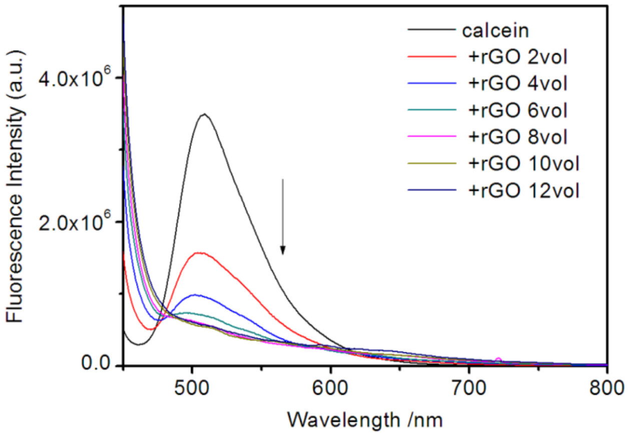


Fig. S10 Fluorescence quenching test of calcein (in solution) by the addition of rGO dispersion with different volumes. Complete fluorescence quenching of calcein occurs.

S2. Related Explanations

S2.1 The rGO content within the rGO@pNIPAM composite is modulated through controlling the rGO/pNIPAM volume ratios of their pristine dispersions during preparation. That is, different volumes of pNIPAM dispersion were added to 1,000 μL rGO dispersion to prepare rGO@pNIPAM composite with different rGO contents.

The rGO content in the composite was determined through calculating the decrease of rGO quantity in the rGO solution after the addition of a certain amount of pNIPAM dispersion. Uv-vis test was used for this. The content of pNIPAM polymer within a pristine pNIPAM microgel particle is 4 wt% while that of water is 96 wt%. As a result, the density of the pNIPAM microgel spheres in water was supposed to be 1 g mL^{-1} in the calculation. A weight percent of rGO in the rGO@pNIPAM composite (without water) was used to describe the rGO content in the composite in the work.

S2.2 After calcein release, the final fluorescence intensity (of calcein) in the pNIPAM particles is observed lower than bulk solution (Figures 6-9). It is inferred that after the calcein release process, the calcein concentration in solvent within the pNIPAM region is comparable to that in bulk solution. However, in consideration of the large part of hydrophobic (isopropyl) groups of pNIPAM polymer, the mean fluorescence intensity of calcein within particle region would present even lower than that in bulk solution.

S2.3 Many parameters, such as molecular weight and concentration, as well as the hydrophilic/hydrophobic properties of end groups, would affect the LCST of pNIPAM [S1,S2]. In this work, the incorporation of inorganic rGO nanoparticles into pNIPAM microgel particles would probably lead to the increase in the LCST of pNIPAM. Such an increase in LCST of a graphene-pNIPAM composite might be ascribed to the high surface area of graphene that could graft/adsorb a large amount of pNIPAM molecules and the immobilization of one end of pNIPAM chain on the surface of graphene. Therefore, the graphene sheet is similar to a cross-linking agent that could affect the conformation change of pNIPAM [S1].

Reference

[S1] J. Dong, J. Weng, L. Dai, Carbon, 2013, 52, 326.

[S2] Y. Xia, N.A.D. Burke, H.D.H. Stover, Macromolecules, 2006, 39, 2275.