

Supporting Information

Experimental Section

Materials

All chemicals used were analytical-reagent grade and used as received. Cetyltrimethylammonium bromide (CTAB), silver nitrate (AgNO_3), sodium borohydride (NaBH_4), ascorbic acid (AA), N-isopropylacrylamide (NIPAM, 97%), glycine (98.5%), N, N'-methylenebisacrylamide (BIS), Crystal violet (CV), Rhodamine 6G (R6G) and 2-2'-azobis (2-methylpropionamide) dihydrochloride (AAPH), were purchased from Shanghai Chemical Reagent Ltd Co. of China. All solutions were prepared using ultrapure water (resistance $> 18 \text{ M}\Omega \text{ cm}^{-1}$).

Synthesis of PNIPAM template and PNIPAM/Ag composites

60ml of ultrapure water was raised to 70°C . The water was purged with nitrogen (15 min), followed by addition of NIPAM (0.6792 g) and BIS (0.1872 g). After 15 min, the nitrogen flow was removed and the polymerization was initiated with the addition of AAPH (800ul 0.1M). After 5-10 min the colorless solution became turbid and the reaction was allowed to proceed for 2 h at 70°C . The white mixture was then allowed to cool down to room temperature under stirring. To remove small oligomers, unreacted monomers, the dispersion was centrifuged (10 min at 8000 rpm) and the precipitate was washed three times with milli-Q water. At last, they were redispersed in 15ml of water. AgNO_3 (300 μl , 0.1M) was added under mild magnetic stirring to 3 ml of PNIPAM spheres. The mixture was kept for 30 min at 25°C to allow Ag^+ to contact with the microgels fully. Then, 150 μL of NaBH_4 0.1M was added to the sample under vigorous magnetic stirring to promote the nucleation of Ag nanoparticles on the PNIPAM surfaces. Silver growth was achieved by adding a mixture composed of CTAB (7.5 ml, 0.2 M), glycine at pH 9.5 (7.5 ml, 0.4 M), and AgNO_3 (2.7 ml, 0.1M) to the previously prepared PNIPAM which surface decorated with Ag nanoparticles seeds. Then, 1.8ml of AA 0.1M was added under vigorous magnetic stirring and the mixture was maintained at 25°C for 30 min, followed by centrifugation (1000 rpm, 10min) to remove excess AA and washing three times with water.

Characterizations

The scanning electron microscopy (SEM) images were taken by a Sirion 200 field emission scanning electron microscope. The transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2010 instrument operated at 100 kV. Dynamic light scattering (DLS) was carried out on a Zetasizer Nano S (Malvern Instruments, Malvern UK) using a detection angle of 173°. The intensity-averaged particle diameter and the polydispersity index values (an estimate of the distribution width) were calculated from cumulative analysis. Ultraviolet-visible (UV-Vis) absorption spectra were collected on a Solidspec-3700 spectrophotometer. SERS of CV and R6G were recorded. Two different experiments were designed. First, 1 mL aliquots of PNIPAM/Ag composites were stabilized at 25°C. Then, 10 µL of analyte was added to each NP suspension reaching final concentrations of 10⁻⁹M. In the first experiment, the corresponding suspension was casting on a silicon slide. Then, the samples were excited with a 532 nm laser line and were collected at different temperatures. In the second experiment, SERS of CV were recorded in suspension by using a macro-sampling accessory equilibration steps were repeated, but starting at 25°C, heating up to 50°C and cooling back to 25°C again. Raman spectra were carried out on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon). The laser beam was focused on the sample in a size of about 1 µm using a 50×microscope objective. The laser power was approximately 1mW and the recording time was 1 s for each spectrum.

Supplementary Figures (1S-8S)

The PNIPAM particles are well separated from each other and the dimmers are all uniform (about 260nm) as shown in Figure 1S.

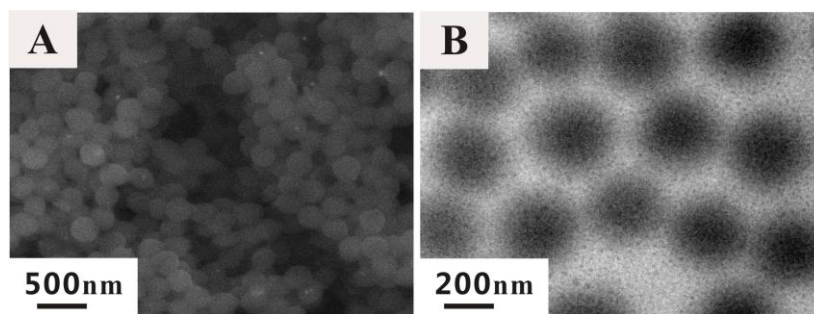


Fig. 1S SEM (A) and TEM (B) images of PNIPAM particles

To test the electrostatic interaction between PNIPAM and Ag nanoparticles, the PNIPAM/Ag composites were washed with water. Fig 2S shows the morphologies of the composites have not any change after three washing and centrifugation, so we conclude that the PNIPAM/Ag composite SERS substrate is stable.

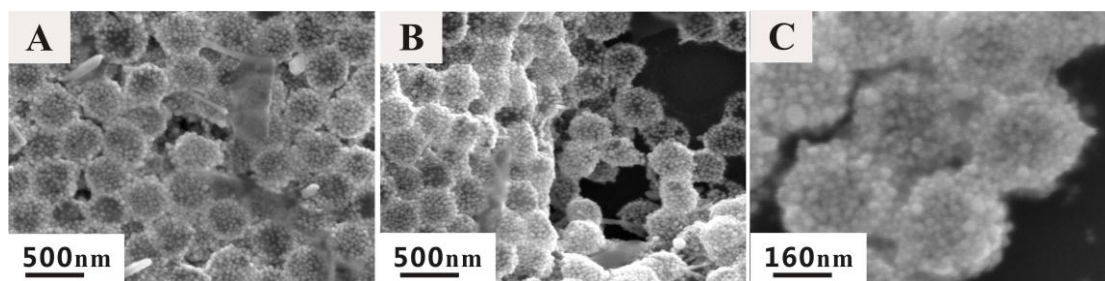


Fig. 2S SEM images of PNIPAM/Ag composite obtained after washing different times with water: (A) one, (B) two and (C) three, respectively.

The typical statistical graph (Fig. 3S (B)) showed that the PNIPAM/Ag composite had the high density hot spots which was estimated by plotting the distance between two particles in the active area of the $0.2 \times 0.2 \mu\text{m}^2$ square patterns of (Fig. 3S (A)). More than 80% of the gap were less than 5nm.¹

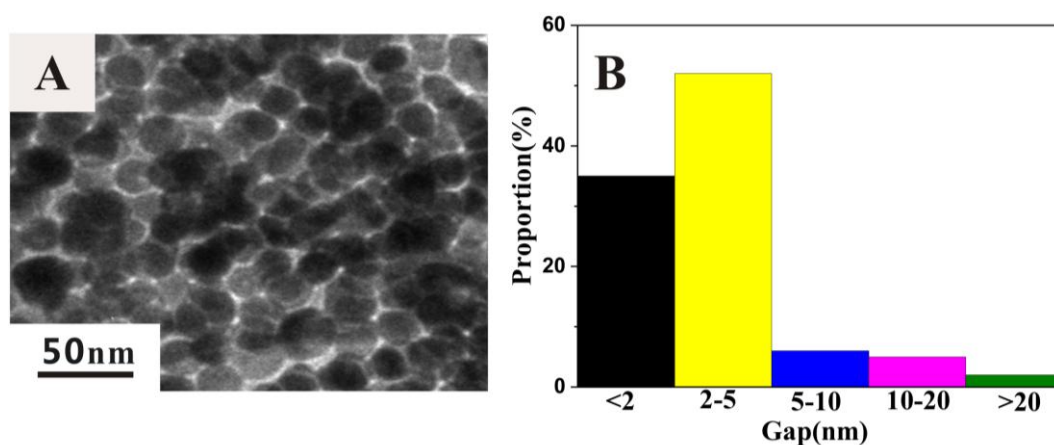


Fig.3S TEM image of enlarged details obtained from one of the PNIPAM/Ag nanosphere (A) and the proportion of hot spots which was estimated by plotting the distance between two particles in the active area of the $0.2 \times 0.2 \mu\text{m}^2$ square patterns (B).

UV-Vis spectra of aqueous dispersions of composite were recorded from 25°C to 55°C. A red-shift from 405 to 424nm of the surface plasmon band of Ag can be observed with increasing temperature due to strong plasmon coupling. This clearly demonstrated that the shrinking of the template drives the decorated Ag nanoparticles closer to each other.^{2,3}

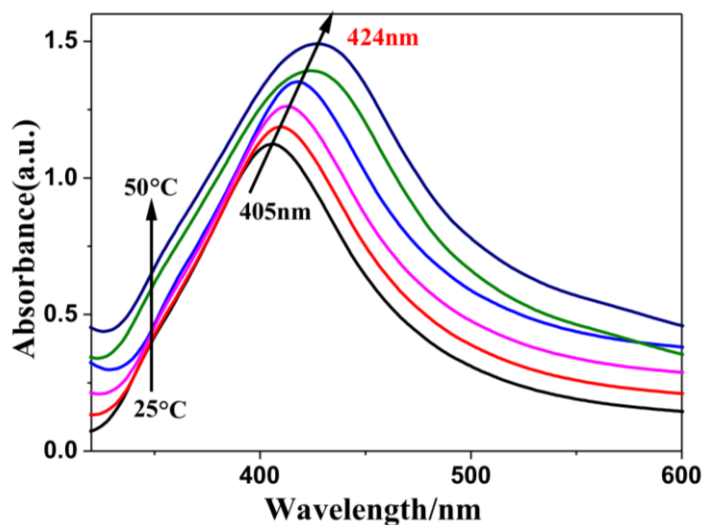


Fig.4S UV-Vis spectra of an aqueous dispersion of PNIPAM/Ag composite at various temperatures (from 25°C to 55°C).

UV-Vis spectra was further utilized to understand the adsorb behavior of PNIPAM microgels and PNIPAM/Ag composites in the probe solutions. The maximum absorbance band at 589nm was chosen to compare. The normalized temporal concentration changes (C/C_0) of CV during the adsorbed process are proportional to the normalized maximum absorbance (A/A_0), which can be derived from the change in the CV absorption profile at a given time interval.⁴ It is observed that pure PNIPAM microgels can adsorb H_2O solvent quickly according to the increased C/C_0 of CV at 1min. Even with the time changed, the C/C_0 is still around 1. But figure 5S (C) and (D) show that the C/C_0 in the pNIPAM/Ag composites decreased quickly at 1min. We know that AA-reduced silver colloids have negative surface charge and CV molecule has positive surface charge so Ag NPs decorated on the surface of microgels can adsorb mass probe molecules because of electrostatic trapping.⁵ The above spectra were all obtained at 25°C. The absorption spectra of CV at the highest temperature (i.e.50°C) was also shown in fig 5S (C). It demonstrated that the temperature nearly has no effects on the adsorbance of composite in CV solution.

It should be noted that the upper curve in Figure 5S (C) is the UV-Vis spectrum of CV. The other curves in Figure 5S(C) are the UV-Vis spectrum of PNIPAM/Ag composite after mixing with CV solution at different time. The peak at around 400 nm is the plasmon peak of silver nanoparticles in the visible light region.

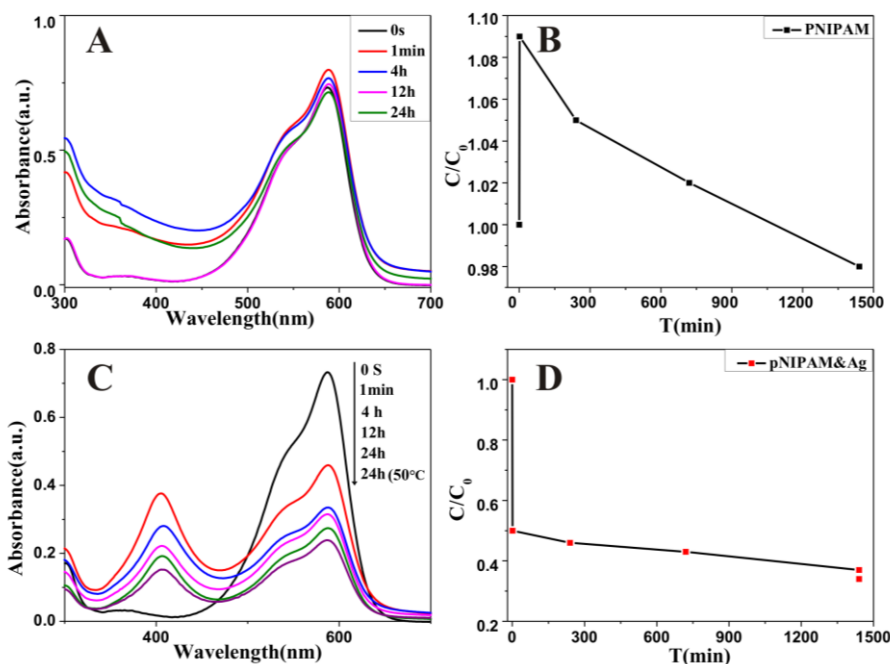


Fig.5S UV-Vis spectra of PNIPAM microgels (A) and PNIPAM/Ag composite (C) after mixing with CV solution at different time and temperature, (B) and (D) are the line relations of (A) and (C), respectively.

It is remarkable that the variations of the SERS intensities observed are fully reversible when switching the temperature below and above the LCST, evidencing a strong and reversible response of the composite system to the external temperature. The details are shown in Figure 6S.

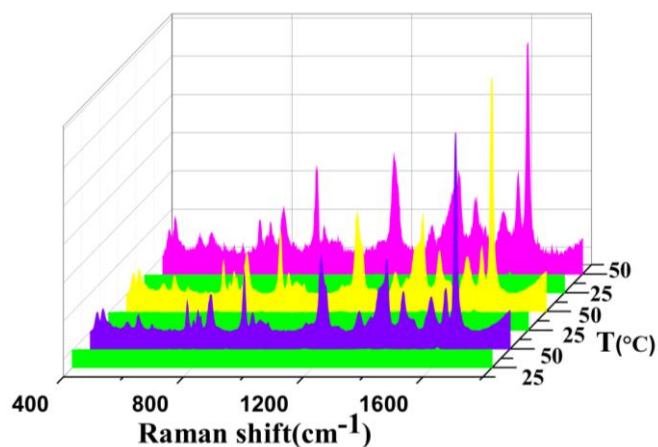


Fig. 6S SERS spectra of CV molecules adsorbed on PNIPAM/Ag substrates and recorded at various temperatures: recycling from 25 to 50 °C and back to 25 °C two times

To further validate the large signal enhancement and high density hot spots structure of our substrate,

we selected the other probe molecule R6G to carry out our experiments. The several hundred times greater SERS AEF of the shrunken state compared with the swollen state was further corroborated by using R6G as the other probe.⁶ The details are shown in Fig. 7S. Using eq0.8, the enhanced multiple is about 876 times.

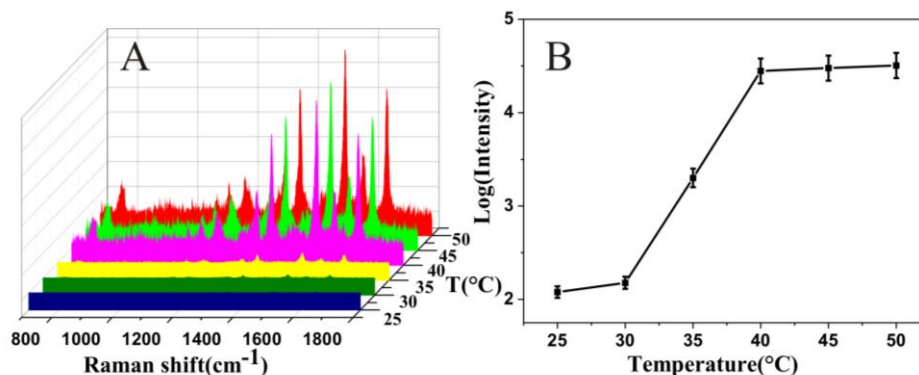


Fig. 7S SERS spectra recorded at various temperatures (below and above the LSCT) of 10⁻⁹ M R6G molecules adsorbed on PNIPAM/Ag substrates; (B) The corresponding relationship between the logarithmic plot of SERS intensity at 1509 cm⁻¹ and temperature together with error bars.

References

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