Electronic Supplementary Information

Probing hidden colloidal transitions with the assistance of surface plasmons

Fangfang Deng, Yunxia Wang, Xiaolin Lu and Tao Ding*

Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education of China, School of Physics and Technology, Wuhan University.
Email: t.ding@whu.edu.cn

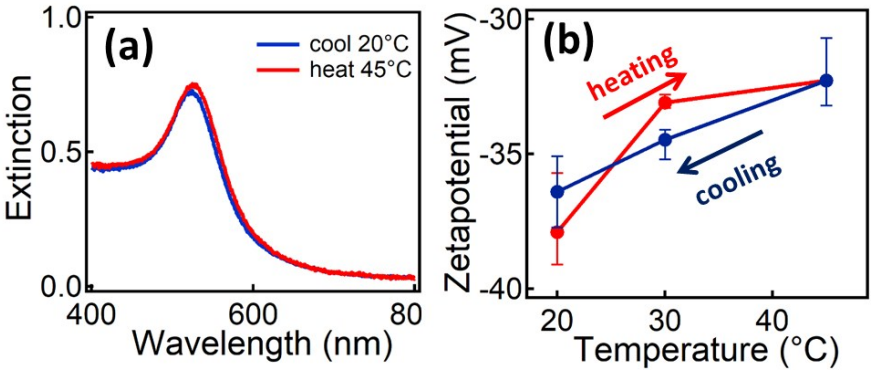

Fig. S1. (a) UV-Vis spectra and (b) zetapotential of Au@PNIPAM-SHCOOH NPs dispersed in aqueous solutions (pH=7) at different temperatures.

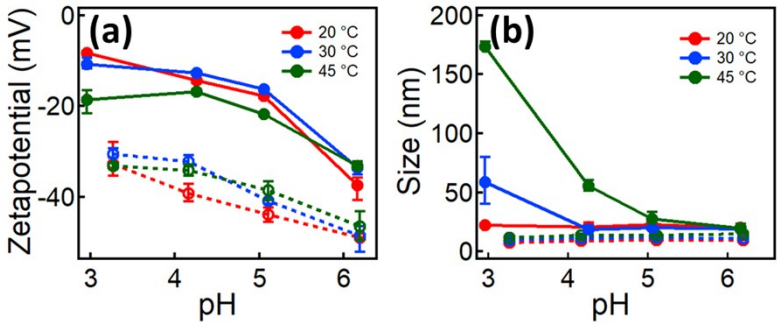

Fig. S2. Zetapotential and hydrodynamic size of Au NPs with and without PNIPAM-SHCOOH. (a) Change of zetapotential with pH at different temperatures. (b) Change of hydrodynamic size with pH at different temperatures. Solid lines represent Au NPs with PNIPAM and dash lines represent Au NPs without PNIPAM (bare citrate Au NPs). The Au NPs with PNIPAM shows slightly larger hydrodynamic size value compared to bare Au NPs, suggesting a coating of PNIPAM as a shielding layer against aggregation.

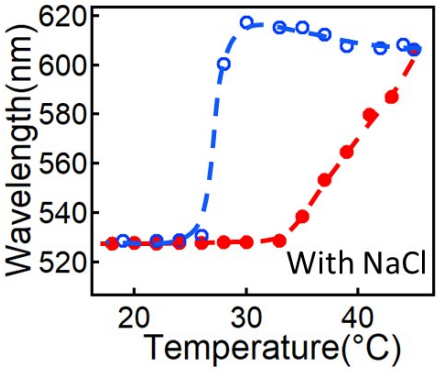

Fig. S3. Spectra response of Au@PNIPAM-SHCOOH NPs solutions containing 0.2 M NaCl: Change of plasmon resonances of with temperature.

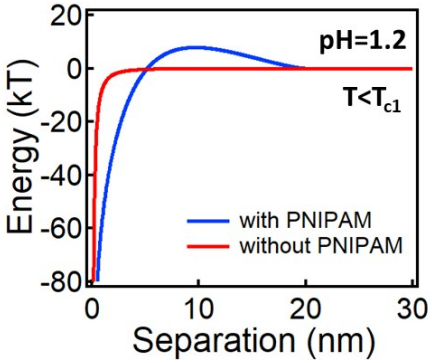

Fig. S4. Energy diagram of Au NPs with and without the presence of PNIPAMSHCOOH at pH=1.2 when the temperature is below the transition temperature T_{c1}.

Energy estimation[1]

The van de Waals interaction and Coulomb screening can be calculated with standard DLVO theory with approximation of Au NPs as two flat Au surfaces.

The elastic/steric energy contributed by compressing/coiling the PNIPAM chains in either the hot or cold states can be estimated from the compression of an elastic sphere against a flat surface.[2]

$$U_e = 5\gamma R^3 \Phi\left(\frac{h}{2R}\right)$$

$$\Phi(x) = \sqrt{x^{-1} - x^2}\left[(1-x)^2 - \frac{4}{9}(1-x)(x^{-1} - x^2) + \frac{4}{45}(x^{-1} - x^2)\right]$$

where *R* is the radius of the sphere., *h* is the height of squished sphere. *γ* is the Young's modulus of PNIPAM, which is 1.8 MPa in swelled state and 13 MPa in globule state. In calculation we estimate the grafting density of PNIPAM on Au NP surface is 10%.

The surface energy of PNIPAM when contact in the hot state estimates that $log(U_{hot}/k_BT) = 0.5$, thus in hot state when $d < t_h$

$$U_s = -3k_BT$$

where t_h is the thickness of the PNIPAM layer when it is in the hot collapsed state. While for cold

state, the hydrophilic PNIPAM chains do not preserve any interactions.

So the total free energy in hot state is

$U_h = U_{vdw} + nU_{cs} + U_e + U_s$

While in cold state, there is negligible elastic potential and no hydrophobic surface energy, the free energy is

$U_c = U_{vdw} + U_{cs} + U_e$

The typical parameter settings used for the calculation are zetapotential (-10 to -15 mV), size of Au NPs: 14nm, thickness of the PNIPAM shells: 20nm in cold state and 3nm in hot state, ion concentration (0.1-0.001 M).

Reference

1. K. J. M. Bishop, C. E. Wilmer, S. Soh, B. A. Grzybowski, *Small* 2009, 5, 1600–1630.
2. A. W. C. Lau, M. Portigliatti, E. Raphaël and L. Léger, *Europhys. Lett.* 2002, 60, 717-723.