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Supporting information

A versatile method for the preparation of poly-acrylamides derivatives functionalized thermo-responsive gold nanoparticles

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Experimental section

Characterization

Molecular weight

We determined the molecular weight and molecular weight distribution of the polymers using GPC and MALDI-TOF MS (Bruker, Autoflex III). The molecular weight measured by GPC was carried on a Hitachi L-2130 pump with a Waters 2410 refractive index detector, and a Waters 2487 ultraviolet detector with the combination of Hersteller MZ-Gel SDplus 5 μm, and the THF was used as eluent at a flow rate of 1.0 mL/min.

Scattering mean diameters

The scattering mean diameters were estimated by dynamic light scattering (DLS) measurements with a Zetasizer Nano ZS (Malvern Instruments). The samples were equilibrated at each temperature for 2 min.

Zeta potential

The zeta potential (ζ) values of the GNPs were measured at 25 ˚C by the Zetasizer Nano ZS Malvern Instruments. The samples for the zeta potential determination were exhaustive dialyzed by water for 24 h.

^{1}H NMR

The nuclear magnetic resonance (^{1}H NMR) spectra were obtained from a Bruker Avance 400 spectrometer (Bruker Bio-Spin, Switzerland) (400 MHz) and the polymers were dissolved in $CDCl_3$.

Transmittance

The transmittance of PNIPAM-2-GNPs and PNIPAM-2 in aqueous solutions changing with temperature was measured by a UV-visible spectrophotometer (UV-2450, Shimadzu, Japan) at 500 nm. The temperature of the cell was controlled by a temperature controller (Shimadzu, Japan) and the heating rate was 1 °C min^{-1} from 34 to 43 °C for PNIPAM-2 and from 33 to 45 °C for PNIPAM-2-GNPs, respectively. The PNIPAM-2 concentration was 1.0 mg mL^{-1}.

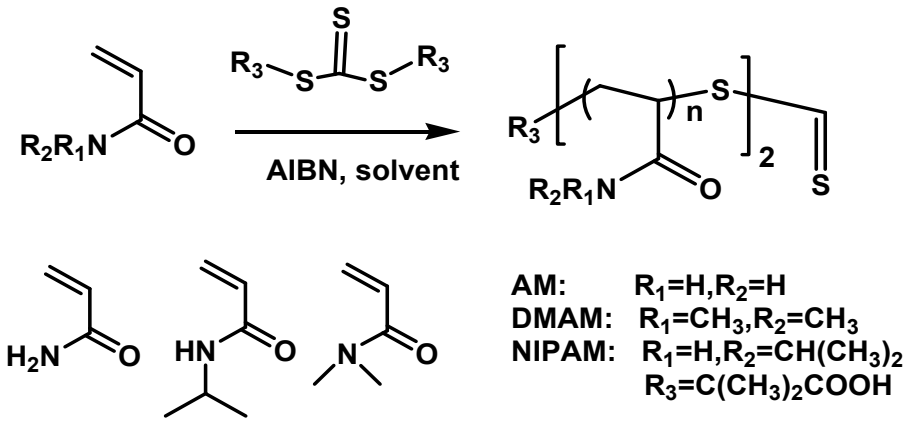
UV-vis absorbance

A UV-vis spectrophotometer (Beijing purkinje general instrument Co. LTD, Beijing) was used for the analysis of the GNPs.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted to measure the thickness of the PNIPAM-2 content on the GNPs. TGA samples were prepared by centrifuging PNIPAM-2-GNPs using a Heal force (Neofuge 23 R, Heal force development Ltd.)

centrifuge at 13,000 rpm for 10 min. The capped particles formed a solid mass at the bottom of the vial, and excess polymer was removed. The remaining particles were washed with water and centrifuged again. This process was repeated 3 times. The particles were placed onto a TGA platinum pan, and the data were collected using a TA Instruments (pyris 1 TGA) at a ramp rate of 20˚C/min to 650 ˚C.



Scheme S1. Synthesis of the poly-acrylamide derivatives.

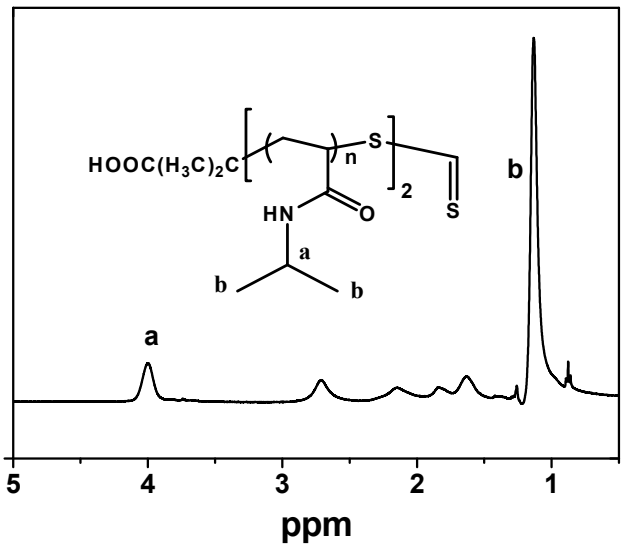


Figure S1 ^{1}H NMR spectra of PNIPAM-2.

Table S1 Physical properties of the polymers

Polymers	Solvent	Polymerization time (h)	Polymerization temperature (℃)	Mn	PDI
PAM	Dioxane	5.5	80	1510 [a]	1.7
PDMAM	THF	22.0	60	1812 [a]	1.3
PNIPAM-1	THF	15.0	60	2255 [b]	1.4
PNIPAM-2	THF	20.0	60	4810 [b]	1.5
PNIPAM-3	THF	24.0	60	10063 [b]	1.7

[a] Mn was obtained by MALDI-TOF; [b] Mn was obtained by GPC

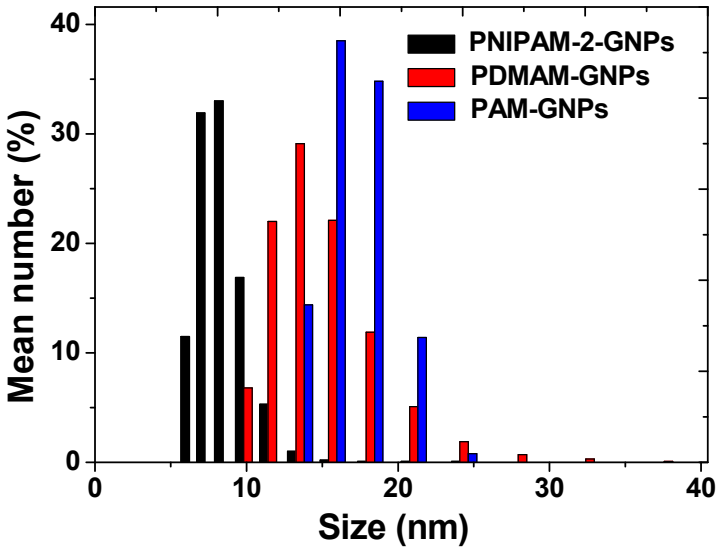


Figure S2 Diameters detection of PNIPAM-2-GNPs (■), PDMAM-GNPs (■) and PAM-GNPs (■) by using DLS (number distributions).

Table S2 Properties of the polymers-GNPs

Polymers-GNPs	Rotation time (h)	AP [a]	Stable time
PAM-GNPs	48	0.20	≥ 1 week
PDMAM-GNPs	1	0.19	≥ 1 months
PNIPAM-2-GNPs	24	0.18	≥ 3 months

[a] AP: aggregation parameter (integrated absorbance between 600 and 700 nm $AP=(A-A_o)/A_o$)

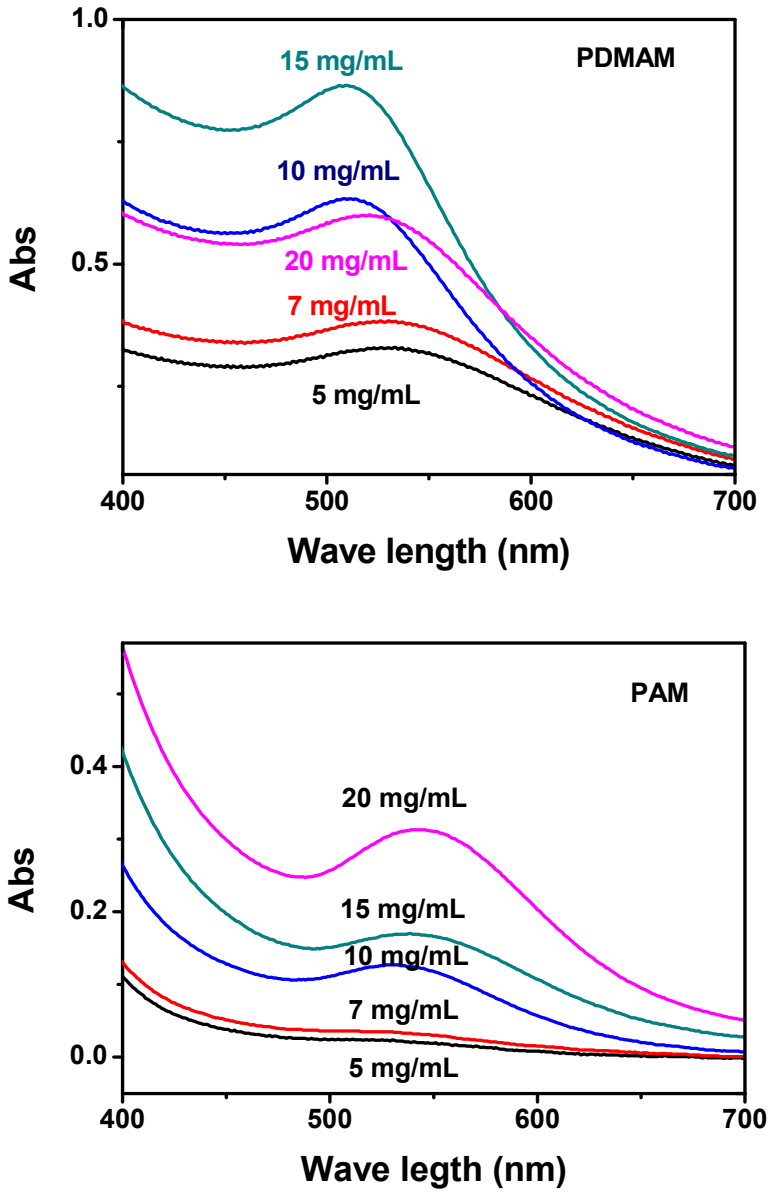


Figure S3 Absorption spectra of PDMAM and PAM prepared GNPs with different concentrations.

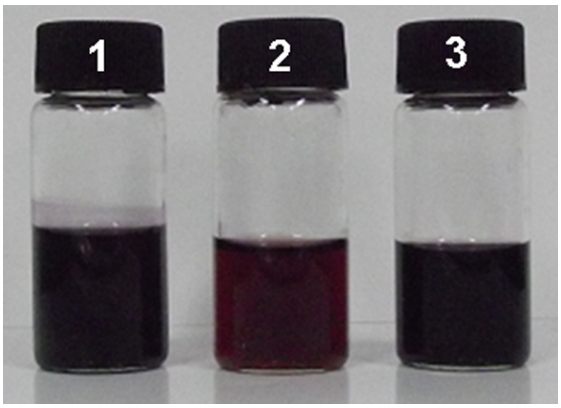


Figure S4 Colorful images of polymer protected GNPs with different molecular weight of PNIPAM (PNIPAM-1: 2225, PNIPAM-2: 4810, PNIPAM-3: 10063).

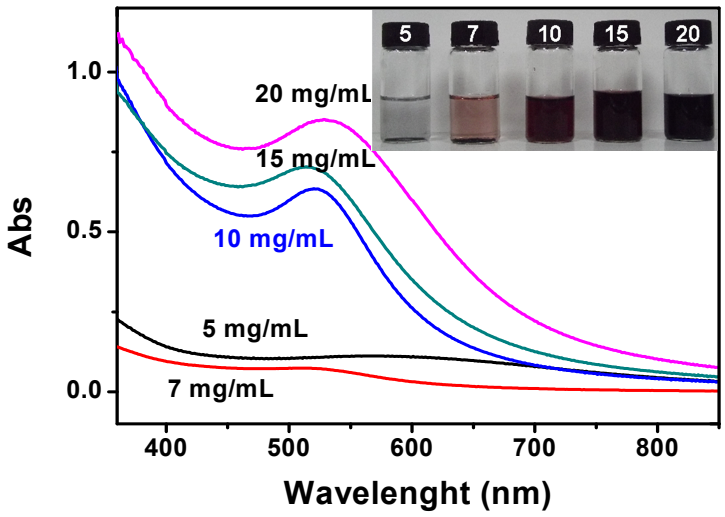


Figure S5 Absorption spectra and colourful images (insert) of PNIPAM-2 prepared GNPs from samples with different concentrations of PNIPAM-2, as labelled.

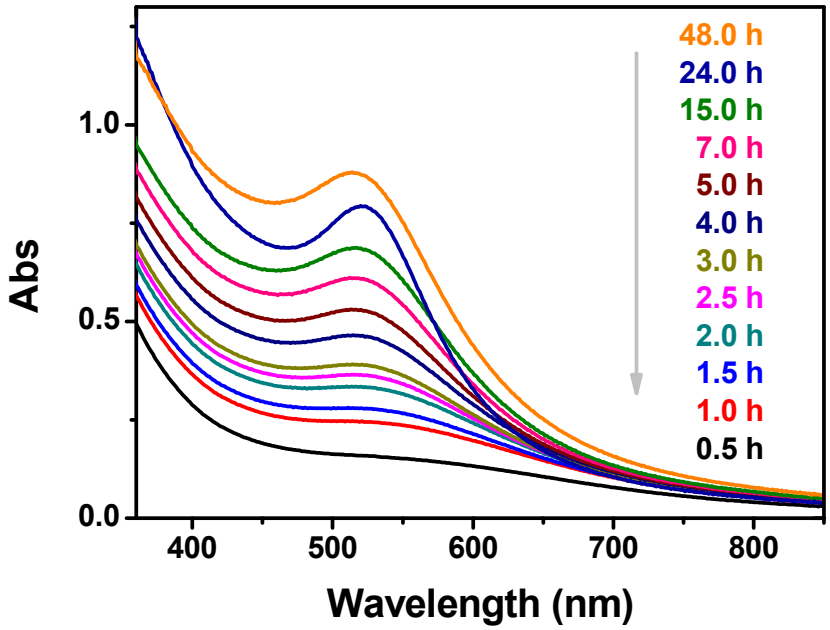


Figure S6 UV-vis absorption spectra of the solution containing PNIPAM-2-GNPs after the increasing of rotation time.

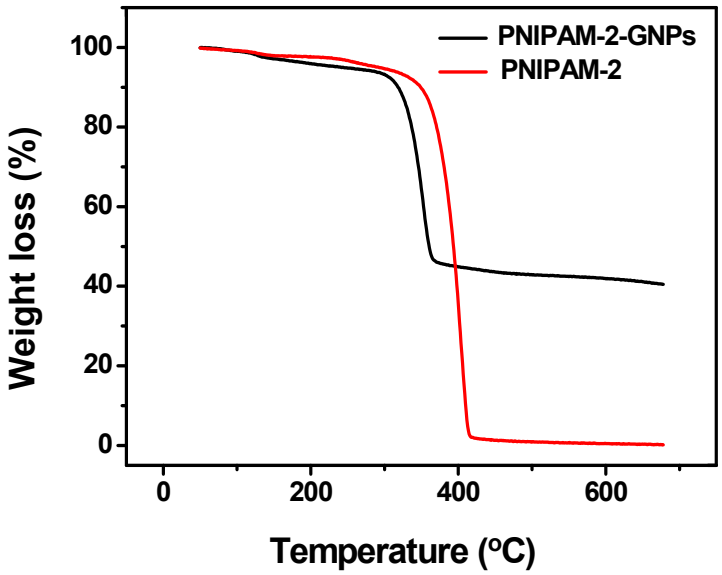


Figure S7 TGA decomposition profiles for the PNIPAM-2 and the PNIPAM-2-GNPs.

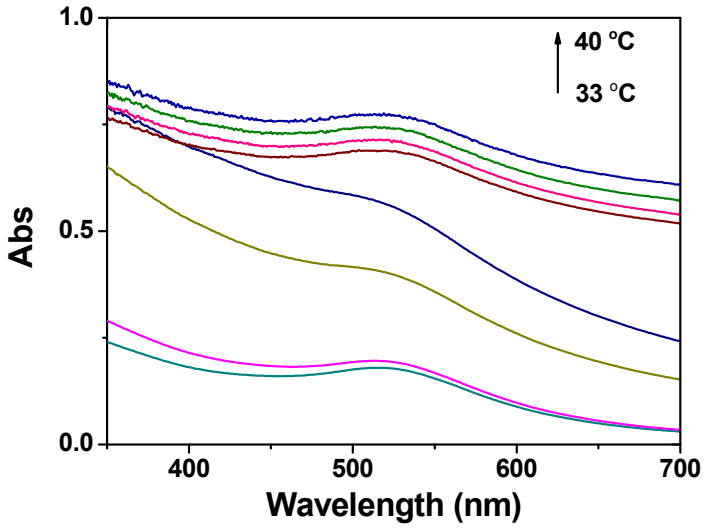


Figure S8 UV-vis absorption spectra of the PNIPAM-2-GNPs solution after the increasing of temperature.

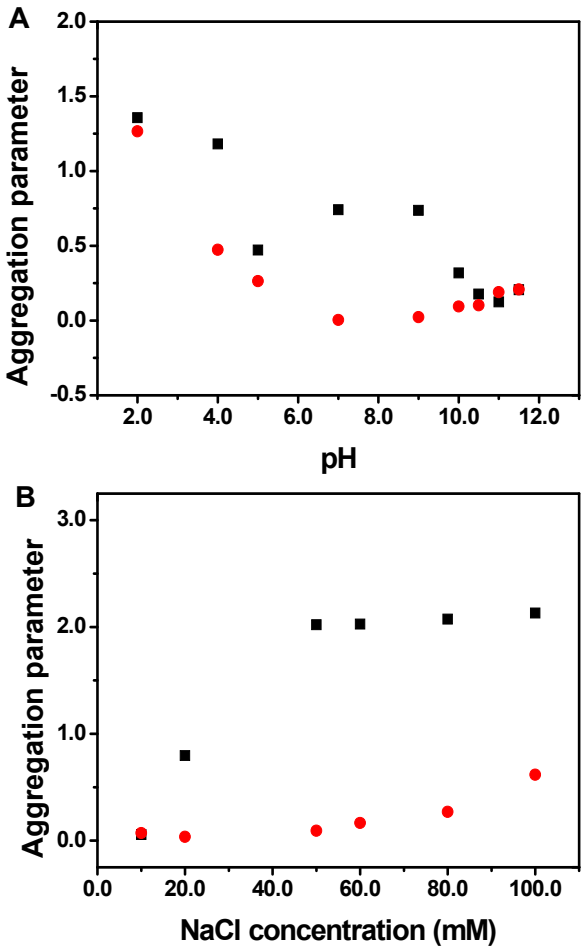


Figure S9 The pH (A) and salt (B) influence on the stability of the PNIPAM-2-GNPs (solid circles ●) and CA-GNPs (solid square ■).

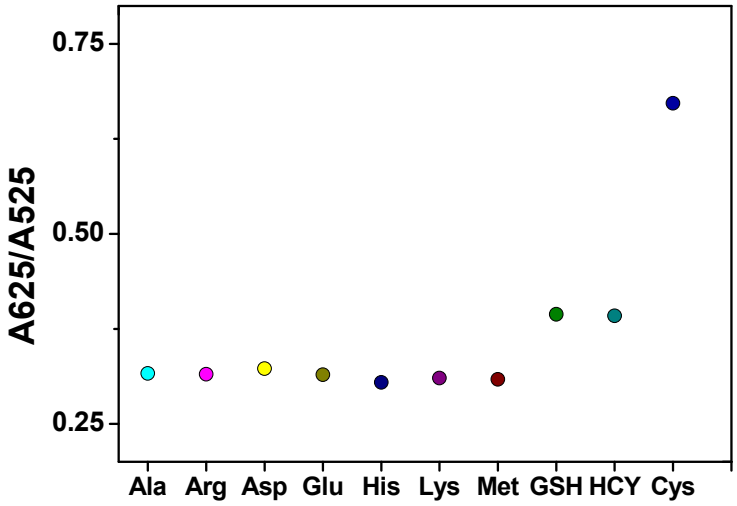


Figure S10 Selectivity of PNIPAM-2-GNPs to Cys and other amino acids. The concentration of Cys, GSH and HCY was 1.0 mM, while other amino acids were 2.0 mM..

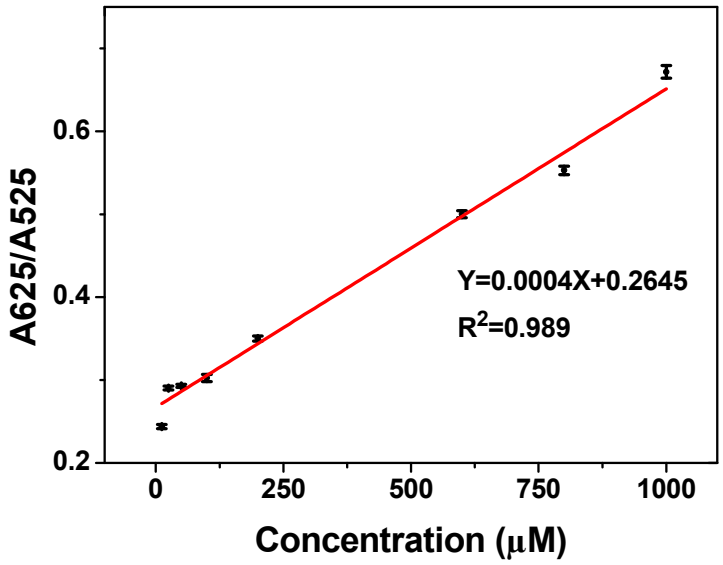


Figure S11 Linear relationship of Cys.