Supplementary information

Poly(*N*-isopropylacrylamide)/Au hybrid microgels: synthesis, characterization, thermally tunable optical and catalytic properties

Shan Shi*, Long Zhang, Tao Wang, Qianman Wang, Yu Gao and Na Wang

College of Materials Science and Engineering, Shenyang University of Chemical Technology, Shenyang 110142, PR China
E-mail: shan.shi@hotmail.com; Fax: +86 24 89388153

Experimental details

Materials

NIPAM (Sigma Aldrich, Inc.) was recrystallized from hexane and dried under a vacuum. AA was distilled under a reduced pressure of nitrogen. Potassium persulfate (KPS) was purified by recrystallization from water. *N, N*-Methylene bisacrylamide (MBA, Alfa Aesar), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC, Alfa Aesar, 98+%) , gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, MP Biomedicals, LLC), 2-aminoethanethiol (AET, RED chemical) and sodium borohydride ($NaBH_4$) were used as received. All reagents were purchased from Sinopharm Chemcial Reagent Co., Ltd., unless otherwise stated. Double-distilled water was used in all experiments.

Synthesis of carboxyl-functionalized PNIPAM microgels

Carboxyl-functionalized PNIPAM microgels were synthesized by soap-free emulsion polymerization of NIPAM and AA within a 500 mL three-necked round bottom flask equipped with a mechanical agitator and a nitrogen inlet. NIPAM monomer (2.0 g), AA monomer (0.2 g), MBA crosslinker (0.2 g), KPS initiator (0.1 g) and water (300 mL) were charged into the flask, stirred (300 rpm) and purged with nitrogen for 30 min. Then, the polymerization was initiated by transferring the flask into a 70^{o}C water bath. The polymerization was continued for 6 h. The obtained microgels was purified by dialyzing against water for 3 days. The dialysate was changed every 12 h.

Preparation of thiol-functionalized PNIPAM microgels

Thiol-functionalized PNIPAM microgels were prepared based on the EDAC-mediated amide bond formation between the carboxyl group of carboxyl-functionalized PNIPAM microgel and amine group of AET. 100 mL of carboxyl-functionalized PNIPAM microgel aqueous disperison (containing 0.8 g solid microgel) and 20 mL of AET aqueous solution (0.2 M) were charged into a 250 mL three-necked round bottom flask and agitated (200 rpm) for 10 min at 20^{o}C. Then, 20 mL of EDAC aqueous solution (0.46 M) was added and the pH value was adjusted to 6.1 with HCl aqueous solution (0.2 M). The reaction was allowed to proceed for 2 h at 20^{o}C under constant agitation. To remove the excess AET, EDAC and other water-soluble substance, the obtained thiol-functionalized PNIPAM microgel dispersion was purified by dialyzing against water.

Preparation of PNIPAM/Au hybrid microgels

20 mL of thiol-functionalized PNIPAM mcirogel dispersion and 0.5 mL $HAuCl_4 \cdot 3H_2O$ aqueous solution (0.025 M) were charged into a 100 mL three-necked round bottom flask and incubated for 3 h at 20^{o}C under constant agitation (200 rpm). Then, 0.5 mL $NaBH_4$ aqueous solution (0.25 M) was rapidly added under vigorous agitation (500 rpm) at 20^{o}C. The reaction mixture turned wine red color immediately, indicating the formation of AuNPs. The obtained PNIPAM/Au hybrid microgels were purified by dialyzing against water.

4-Nitrophenol reduction catalyzed by PNIPAM/Au hybrid microgels

The thermally tunable catalytic property of PNIPAM/Au hybrid microgels was investigated via the reduction of 4-nitrophenol (4-NP) with $NaBH_4$ at different temperatures. Into a quartz cell for UV-vis spectroscopy, 1 mL of 4-NP aqueous solution (0.1 mM) and 2 mL $NaBH_4$ aqueous solution (20 mM) were added and adjusted to the desired temperature. At the same time, the PNIPAM/Au microgel latex was also adjusted to the desired temperature in a water bath for 10 min. Then, 0.5 mL of PNIPAM/Au latex (0.06 mg/mL) was added to the quartz cell and the UV-vis spectra were recorded immediately at a given time interval.

Characterization

Dynamic light scattering (DLS) measurements were made to determine the hydrodynamic diameter (D_h) using a zeta potential analyzer (ZetaPlus, Brookhaven Instruments Corporation) equipped with a 15 mW solid state laser (678.0 nm) as light source. The scattered light was measured at the angle of 90° and collected by the autocorrelator. The measurements were made after allowing 5 min for sample equilibration at each temperature.

Transmission electron microscopy (TEM) was carried out to observe the morphology of samples using a JEM-1200EXII microscope (JEOL). The microgels were sufficiently diluted with water and dropped onto a carbon film supported on a standard copper mesh grid. After being dried at 50 °C, the specimens were examined by TEM at an accelerating voltage of 100 kV. In the case of PMMA/Au hybrid microgels, the number-average diameter (D_n) and weight-average diameter (D_w) of AuNPs were calculated by counting at least 100 individual particles from the TEM images, according to the following equations:

$$D_n = \frac{\sum n_i D_i}{\sum n_i}$$

$$D_w = \frac{\sum n_i D_i^4}{\sum n_i D_i^3}$$

where n_i is the number of the particles having diameter of D_i.

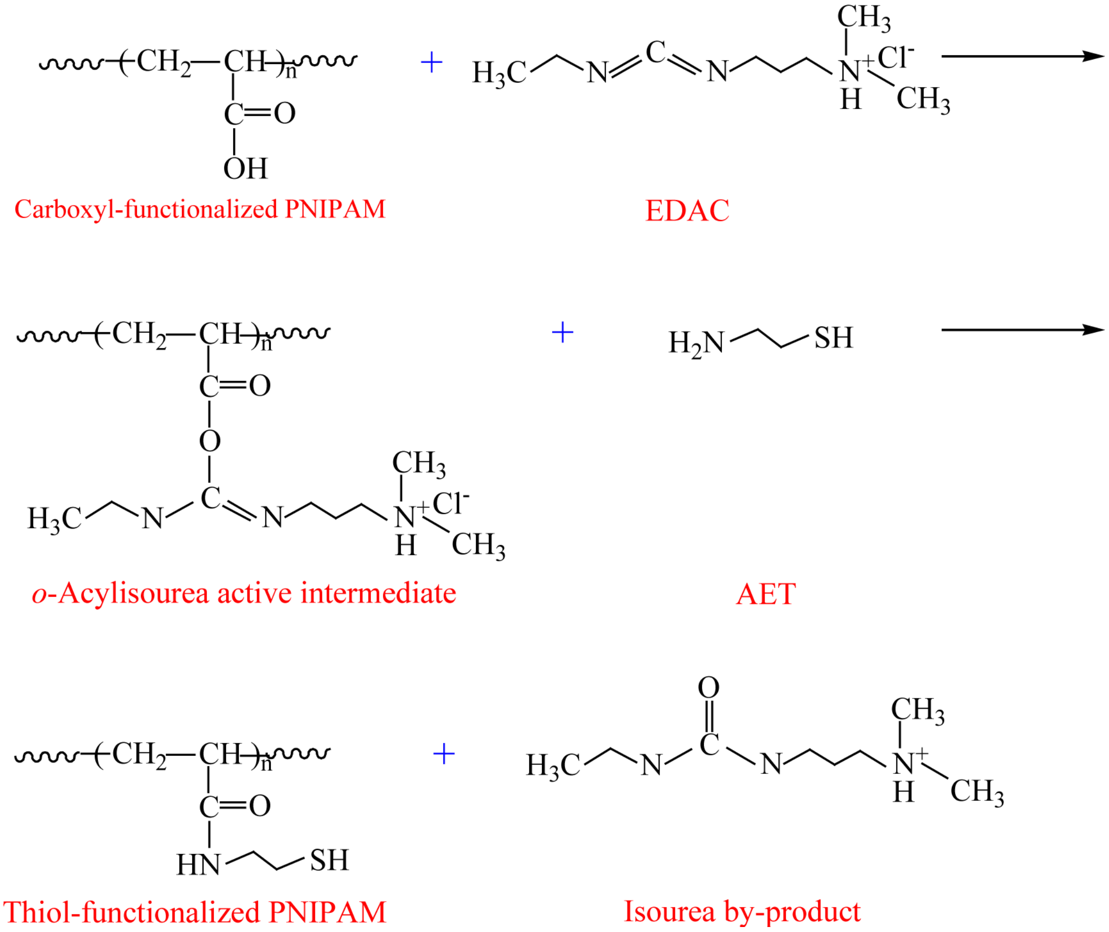
Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a Nicolet iS10 spectrometer using the pressed-KBr-pellet technique. The spectra were scanned over the range of 4000-400 $\mathrm{cm^{-1}}$.

UV-visible (UV-vis) spectroscopy was performed on a Shimadzu UV-2450 spectrometer equipped with a temperature controller (TCC-240A).

Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60H instrument at a heating rate of 10 °C/min under nitrogen atmosphere (50 mL/min).

Elemental analysis was carried out on a Flash EA1112 apparatus (Thermo Finnigan).

Supplementary Scheme and Figures



Scheme S1 Detailed reaction process for the preparation of thiol-functionalized PNIPAM microgels using EDAC-mediated amide bond formation between carboxyl-functionalized PNIPAM microgels and AET.

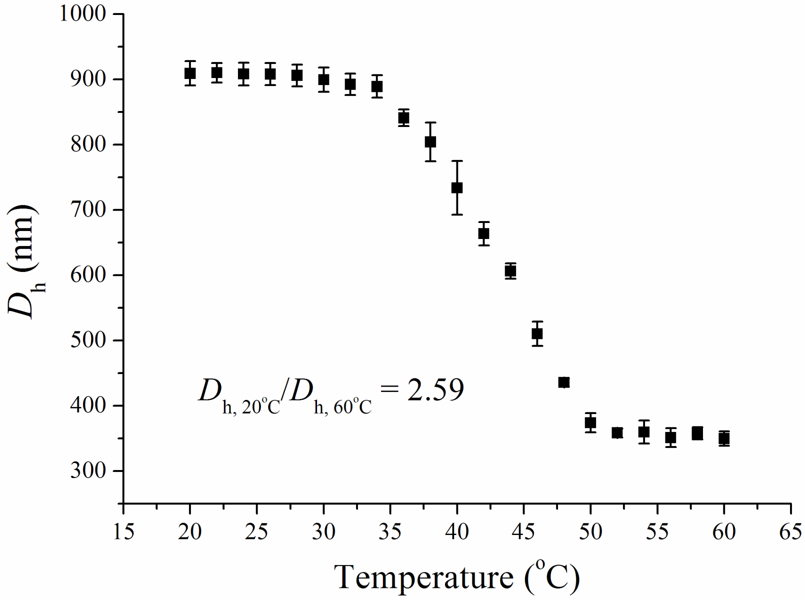


Fig. S1 Plot of D_h of carboxyl-functionalized PNIPAM microgels *versus* temperature. Error bars are the standard deviation of the mean diameter averaged over three measurements.

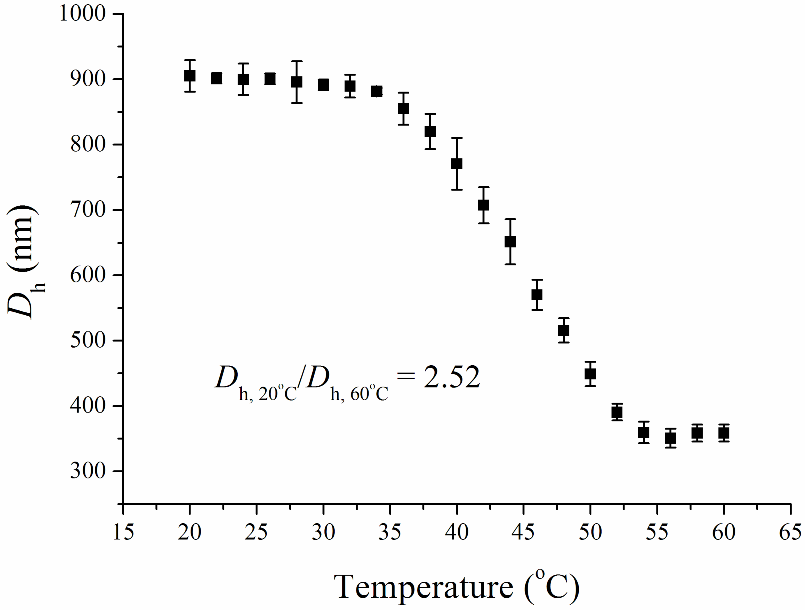


Fig. S2 Plot of D_h of thiol-functionalized PNIPAM microgels *versus* temperature. Error bars are the standard deviation of the mean diameter averaged over three measurements.

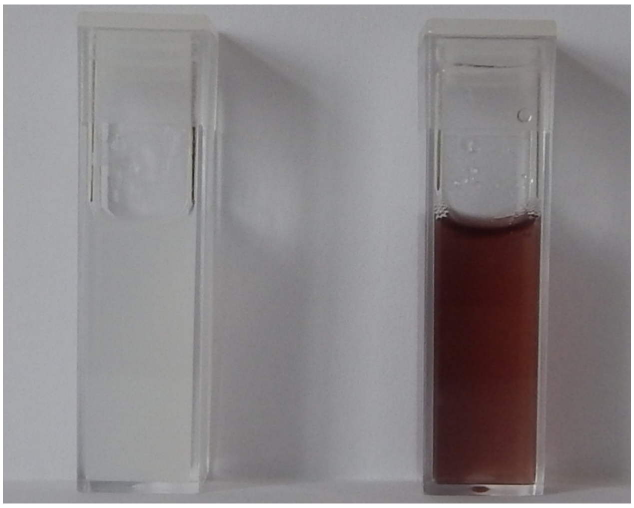


Fig. S3 Photographs of thiol-functionalized PNIPAM microgels (*left*) and PNIPAM/Au hybrid microgels (*right*).

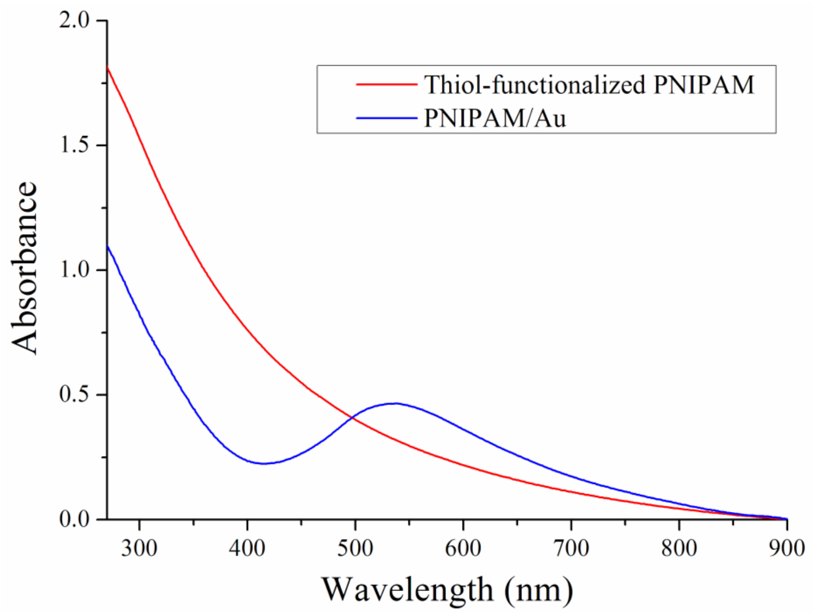


Fig. S4 UV-vis spectra for the thiol-functionalized PNIPAM microgels and PNIPAM/Au hybrid microgels (20°C).

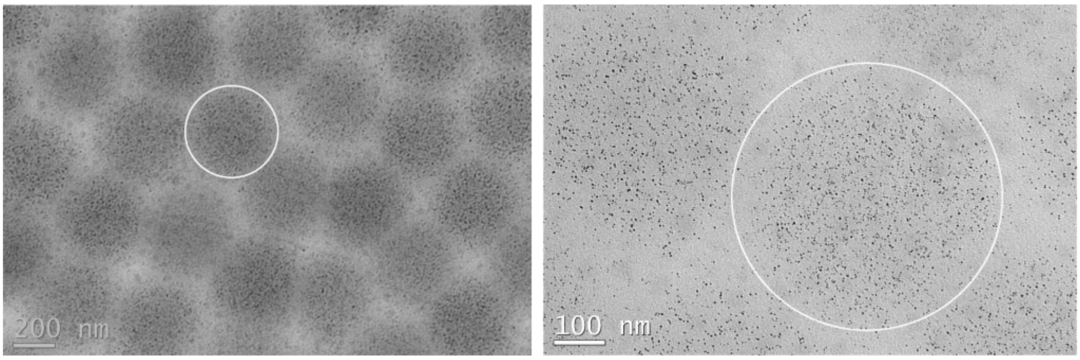


Fig. S5 TEM images for PNIPAM/Au hybrid microgels at lower magnifications. The white circles indicate two single hybrid microgels.

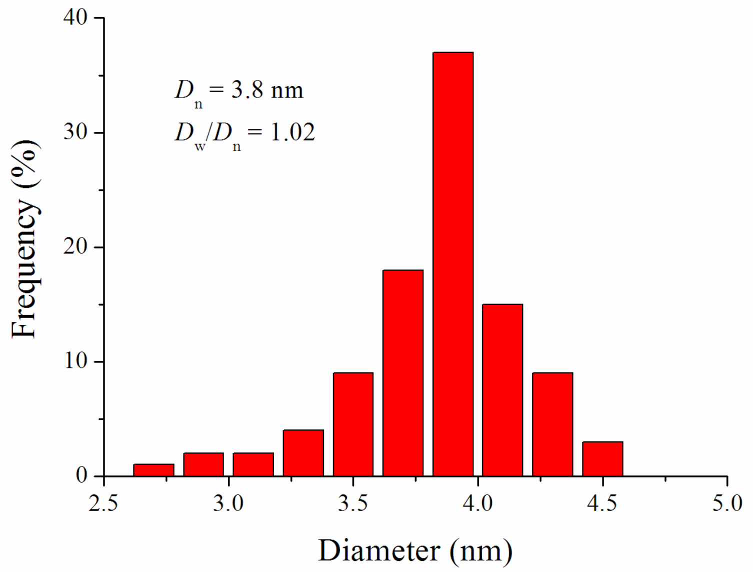


Fig. S6. Size distribution histogram for AuNPs loaded within the hybrid microgels.

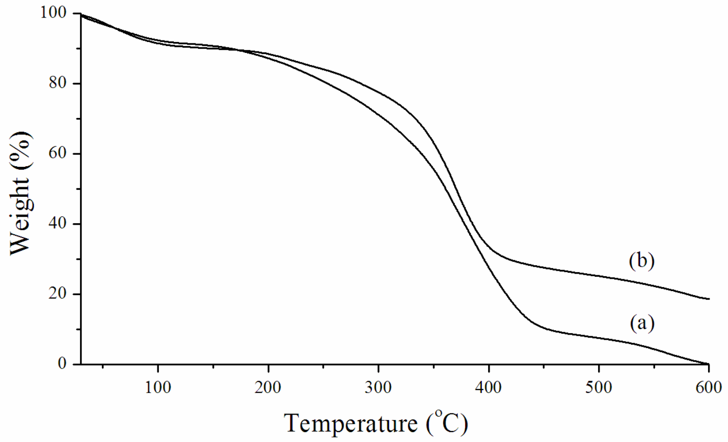


Fig. S7 TGA curves for (a) thiol-functionalized PNIPAM microgels, and (b) PNIPAM/Au hybrid microgels.

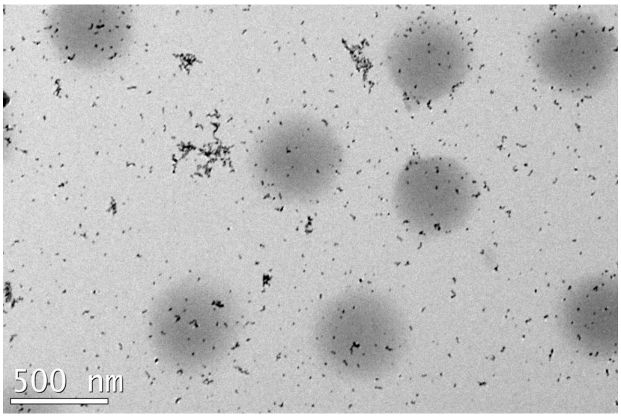


Fig. S8 TEM image for the product obtained from the control experiment using carboxyl-functionalized PNIPAM to replace thiol-functionalized PNIPAM microgels (while maintaining other conditions unchanged) in the *in situ* reduction of $HAuCl_4$ by $NaBH_4$.

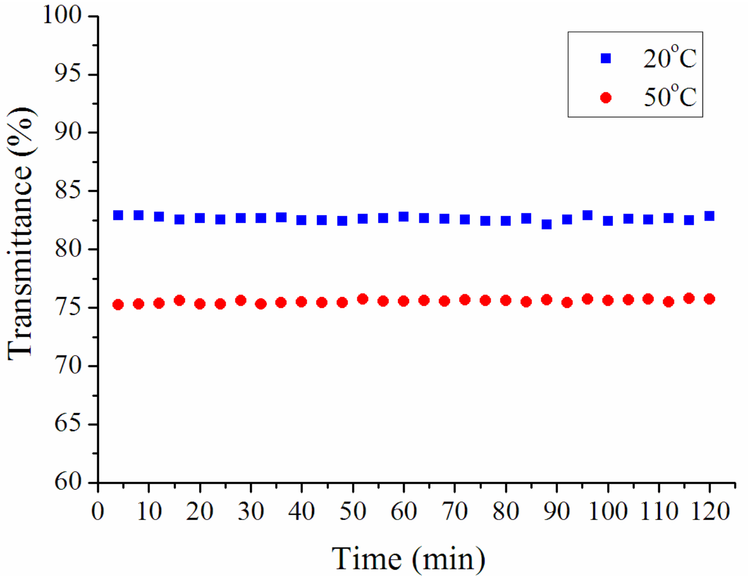


Fig. S9 The transmittance change of PNIPAM/Au hybrid microgel dispersion (0.4 mg/mL) with storage time, determined by UV-vis spectroscopy at a wavelength of 500 nm.

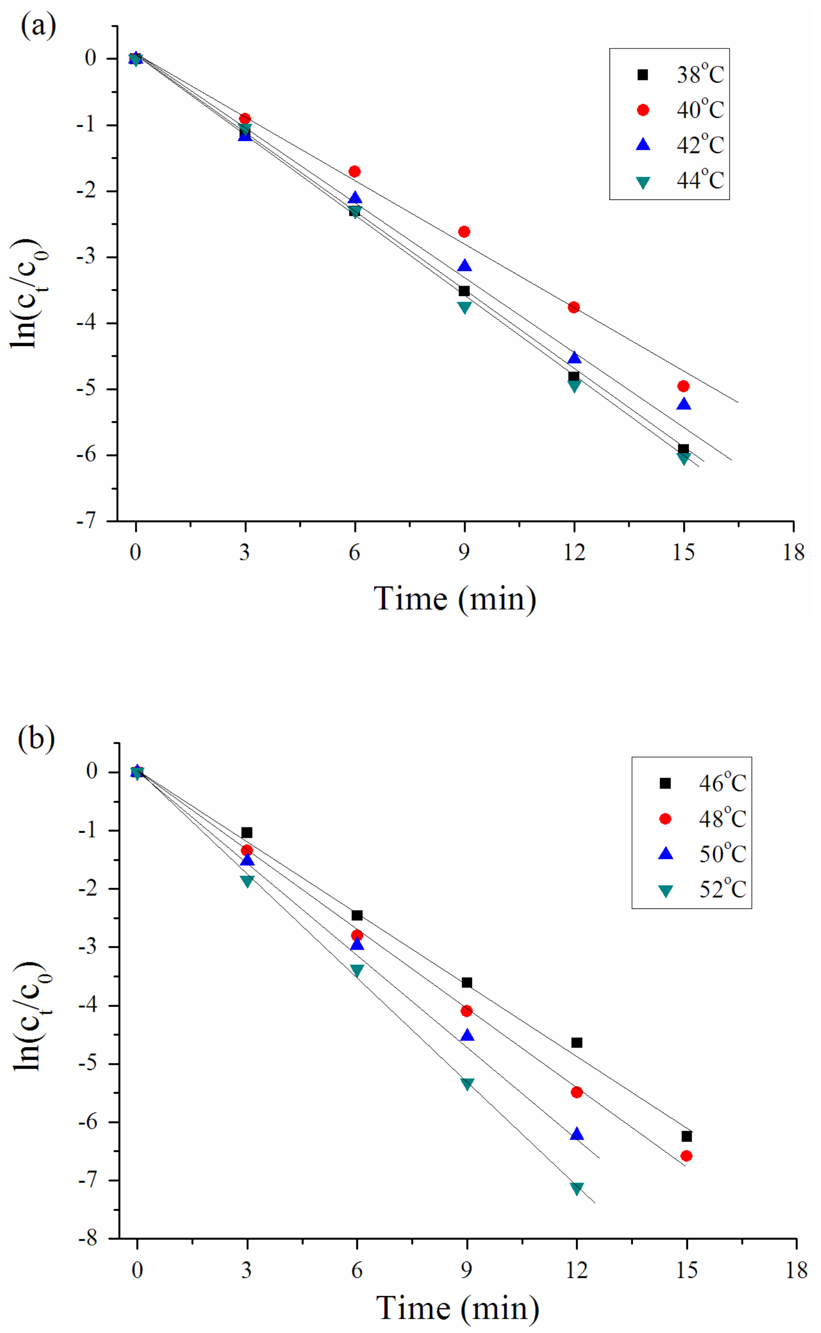


Fig. S10 Plot of ln(c_t/c_0) *versus* time for the reduction of 4-NP to 4-AP catalyzed by PNIPAM/Au hybrid microgels at temperatures of (a) 38-44°C, and (b) 46-52°C.