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Thermo-sensitive Microgels Supported Gold Nanoparticles as Temperature-mediated Catalyst

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 Electronic Supplementary Information

Abstract Microgels with a thermo-sensitive poly(*N*-isopropylacrylamide) (polyNIPAm) backbone and bis-imidazolium (VIM) ionic cross-links, denoted as poly(NIPAm-co-VIM), were successfully prepared. The as-synthesized ionic microgels were converted to nanoreactors, denoted as Au@PNI MGs, upon generation and immobilization of gold nanoparticles (Au NPs) of 5–8 nm in size into poly(NIPAm-co-VIM). The content of Au NPs in microgels could be regulated by controlling the 1,6-dibromohexane/vinylimidazole molar ratio in the quaternization reaction. The microgel-based nanoreactors were morphologically spherical and uniform in size, and presented reversible thermo-sensitive behavior with volume phase transition temperatures (VPTTs) at 39–40 °C. The Au@PNI MGs were used for the reduction of 4-nitrophenol, of which the catalytic activity could be modulated by temperature.

Keywords Microgel; Thermo-sensitive; Gold nanoparticle; Catalyst

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INTRODUCTION

Nitro-aromatic compounds, derived from the industrial manufacturing processes of pesticides, herbicides and synthetic dyes, are considered as one of the most refractory water pollutants with high toxicity.^[1,2] Most of the nitrophenols have been classified as priority pollutants by United States Environmental Protection Agency (US EPA),^[3] among which 4-nitrophenol (4-NP) is listed as a notorious and representative organic pollutant. By reduction of 4-NP into 4-aminophenol (4-AP), which is used as corrosion inhibitor, photographic developer, drying agent, important precursor or intermediate for preparation of drugs or chemicals, this problem can be mitigated.^[4,5]

So far, the most efficient method for the reduction of 4-NP into 4-AP is to use NaBH₄ and metal nanoparticles (NPs) as reductant and catalyst, respectively. Metal nanoparticles such as Au,^[6] Ag,^[7] Pt,^[8] Pd,^[9] Cu,^[10] Ni,^[11] and Fe^[12] have been prepared and investigated as catalysts. Among them, Au NPs show high catalytic activity under mild conditions and have attracted much attentions.^[4,13] In general, the catalytically

active sites sit on the surface of the NPs.^[3] Therefore, smaller particles possessing a higher surface-to-volume ratio are more catalytically active than large ones with the same mass.^[2,14] However, smaller Au NPs generally tend to minimize their surface energy by aggregation thus lower down catalytic activity.^[15,16] For example, Sun *et al.*^[17] reported that the colloidal metal NPs flocculated during a catalytic process, which depressed the catalytic activity and selectivity. Upon advances in nanotechnology, a wide range of carriers have been investigated to stabilize metal NPs for catalysis, such as silica,^[3] graphene,^[5] polymeric spheres,^[18] *etc.*

Microgels are microscopic 3D cross-linked polymer networks swollen with any appropriate solvent.^[19–21] Functional monomers can be easily incorporated into the microgels *via* copolymerization with crosslinker, so that the stimuli-responsiveness of the polymer network can be adjusted *in situ*.^[22] In response to external stimuli, such as temperature, pH, ionic strength, *etc.*, microgels show reversible swelling and deswelling characteristics.^[23] In a collapsed state, they can behave as hard colloids, while soft in a swollen state.^[24] Poly(*N*-isopropylacrylamide) (PNIPAm) microgel is one of the most studied temperature-responsive microgels, which exhibits a volume phase transition temperature (VPTT) at ~32 °C.^[25,26] Such stimuli-responsive microgels with long-term stability in aqueous solution or other proper solvents have been applied in catalysis, drug delivery, tissue engin-

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engineering, cosmetics, and sensing.^[27–31] Therefore, microgels could be a suitable candidate as a carrier to prevent aggregation of Au NPs, and at the same time bring them controllable stimuli responsiveness.

Recently, a series of thermo-sensitive PNIPAm microgels with bis-imidazolium ionic liquid cross-linking structure were developed by us *via* surfactant free emulsion polymerization (SFEP).^[32,33] In the present work, the thermo-sensitive ionic microgels were loaded with Au NPs after the immobilization and reduction of AuCl_4^- anions, as shown in Scheme 1. The thermo-sensitive poly(*N*-isopropylacrylamide-*co*-imidazolium) microgels loaded with Au NPs (Au@PNI MGs) were used as temperature-mediated catalyst for the reduction of 4-NP by NaBH_4 . The loading of Au NPs into the microgels, on the one hand, could increase the dispersion stability of Au NPs in water; on the other hand, the thermo-sensitivity of the microgel could regulate the contact between Au NPs and the external environment, *e.g.*, the substrate molecules. Since hydrogen can be generated during the catalytic reaction,^[34,35] such temperature-mediated catalyst may have promising potential in controllable micromotors.

EXPERIMENTAL

Materials and Chemicals

N-isopropylacrylamide (NIPAm, 98%), 1-vinylimidazole

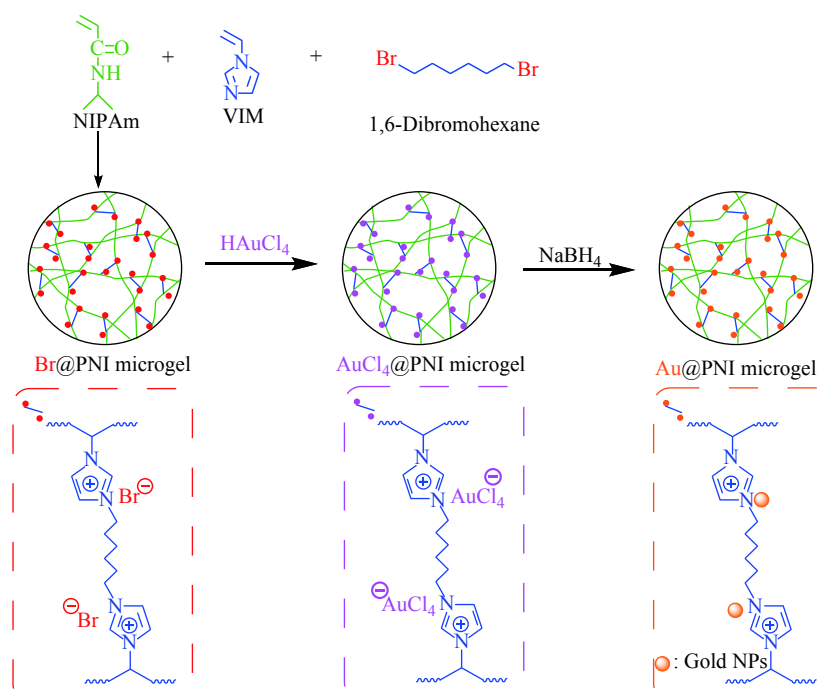
(VIM, 97%), 2,2'-azobis(2-methylpropionamide) dihydrochloride (AIBA, 99%), and 4-nitrophenol (4-NP, 99%) were purchased from J&K Chemicals, China. 1,6-Dibromohexane (99%) was purchased from Tokyo Chemical Industry Co. Ltd, Japan. Sodium borohydride (NaBH_4 , 98%) was purchased from Acros Organics, Belgium. Chloroauric acid (HAuCl_4 , 41.8 wt%) was purchased from Innochem, China. Sodium citrate (99%) was purchased from Sinopharm Chemical Reagent Co. Ltd, China. All the reagents were used as received. Deionized water was used throughout the experiments.

Fabrication of the PNI Microgels

The thermo-sensitive ionic microgels were prepared and purified according to our previous method.^[33] NIPAm, VIM, and 1,6-dibromohexane were used as main monomer, comonomer and cross-linker, respectively. The preparation conditions are listed in Table 1. The sample codes were named according to the following example: for PNI-1/2, 'P', 'N', and 'I' represented poly, NIPAm, and VIM, respectively. The numeric of '1/2' presented the molar ratio of bromo groups in 1,6-dibromohexane to imidazole moieties in VIM. The yields of PNI microgels were about 72%–81%.

Preparation of the Microgel-supported Gold Nanoparticles

Gold nanoparticles were synthesized *in situ* in PNI microgels, by using the quaternary ammonium cationic sites in the micro



Scheme 1 Synthetic route towards Au@PNI microgels *via* surfactant free emulsion polymerization, anion exchange and reduction

Table 1 Preparation conditions and results of thermo-sensitive ionic microgels

Sample	NIPAm (mmol)	VIM (mmol)	1,6-Dibromohexane (mmol)	D_{DLS}^a (nm)	D_{TEM}^b (nm)	Content of Au NP		Swelling ratio ^{c}	VPTT ($^{\circ}\text{C}$)
						C_{TGA}^c	C_{EDS}^d		
PNI-1/2			0.075	634.3 ± 11.6	467 ± 27	7.1%	8.3%	7	39
PNI-2/3	2	0.3	0.1	420.9 ± 10.9	278 ± 14	17.5%	16.3%	5	40
PNI-1			0.15	358.2 ± 5.6	265 ± 25	21.3%	22.1%	3	40

^a Measured at 25 $^{\circ}\text{C}$ by DLS; ^b Counted from TEM images; ^c Measured by TGA (wt%); ^d Measured by EDS (wt%); ^e The ratio of microgel volume at 25 $^{\circ}\text{C}$ to the reference volume at 70 $^{\circ}\text{C}$, *i.e.* V_{25}/V_{70} , measured by DLS

gels for particle nucleation and growth, as shown in Scheme 1. 30 mg of HAuCl₄ (41.8 wt% of Au) was added into 40 mL of PNI microgels suspensions (1 mg·mL⁻¹), and the mixture was stirred for 2 h. The excess AuCl₄⁻ was removed by dialysing against deionized water for 1 day. Then, the suspensions were cooled to 0 °C and bubbled with N₂ for 30 min. Thereafter, 5 mL of NaBH₄ aqueous solution (12 mg·mL⁻¹) was added dropwise into the solution under stirring and reacted for 1 h to form Au NPs in the PNI microgels (Au@PNI MGs). The microgel-supported Au NPs were purified by several centrifugations and redispersion processes with the supernatant replaced by deionized water.

Synthesis of Gold Nanoparticles in Aqueous Solution

Synthesis of Au NPs in aqueous solution was performed by using the method reported in the literature.^[36] Briefly, 45 mL of chloroauric acid aqueous solution (HAuCl₄, containing 5 mg of Au) was heated to the boiling point, then 5 mL sodium citrate aqueous solution (containing 24.7 mg of sodium citrate, 1%) was added with stirring. After about 8 min, deep wine-red color appeared gradually. The obtained Au NPs were collected by several centrifugations and redispersion processes with the supernatant replaced by deionized water.

Catalytic Reduction of 4-Nitrophenol

The reduction of 4-nitrophenol (4-NP) was conducted in a standard quartz cell and monitored by a UV-Vis spectrometer. In a typical process with Au@PNI microgels as catalyst, 1 mL of fresh NaBH₄ aqueous solution (3 mg·mL⁻¹) was mixed with 1 mL of 4-NP aqueous solution (0.12 mmol·L⁻¹) in a quartz cuvette. Given amounts of Au@PNI MGs or Au NPs aqueous solutions were mixed with the deionized water to make a total volume of 1 mL, and then added to quartz cuvette as catalyst. Then UV-Vis spectra of the solution were immediately recorded every 30 s in the range of 200 nm to 550 nm. Since NaBH₄ reacts much faster with oxygen dissolved in water than 4-NP, the catalytic reduction does not start immediately.^[37] To avoid induction period, the dissolved oxygen was removed by purging with nitrogen for 30 min before catalytic reduction.

Recovery and Reuse of the Catalyst

The catalyst of Au@PNI MGs was recovered by several centrifugations and redispersion processes with the supernatant replaced by deionized water to remove all the reactants. The recovered Au@PNI MGs were reused in another run with the same catalytic reaction conditions.

Characterization

The morphology and particle sizes of microgels and Au NPs were determined by transmission electron microscopy (TEM, JEOL JEM-1200) and scanning electron microscopy (SEM, HITACHI S4800). The samples for SEM were coated with platinum vapors before observation. The hydrodynamic diameters and thermo-sensitive behaviors of the microgels were determined by dynamic light scattering (DLS, Brookhaven 90 Plus Particle Size Analyzer). The composition of the microgels was analyzed by X-ray energy dispersive spectroscopy (EDS, HITACHI S4800) and thermo-gravimetric analyses (TGA, PerkinElmer PYRIS 1). The samples were not treated with gold or platinum vapors before the EDS measurement. TGA measurements were

performed under dry N₂ at a flow rate of 100 mL·min⁻¹. The oven temperature was raised from room temperature to 800 °C at a rate of 10 °C·min⁻¹. UV-Vis spectroscopy was performed on a Cary 100 instrument (Varian Australia Pty Ltd.) equipped with a temperature controller.

RESULTS AND DISCUSSION

Synthesis and Characterization of Microgel-supported Gold Nanoparticles

The microgels with thermo-sensitive poly(*N*-isopropylacrylamide) (PNIPAm) as backbone and quaternary imidazolium cations in cross-linking sites were reported previously.^[33] Such microgels are suitable nanoreactor to immobilize metal nanoparticles.^[38,39] The counterions of quaternary ammonium cations in cross-linking network of microgels, *i.e.* Br⁻, could be substituted with AuCl₄⁻ by anion exchange reaction. The latter could be further reduced to form Au NPs by sodium borohydride in cross-linking sites of the microgels, as shown in Scheme 1. Fig. 1 shows the typical TEM images of the Au NPs loaded microgels, where spherical particles with narrow size distribution could be observed. The average diameters of Au@PNI-1/2, Au@PNI-2/3, and Au@PNI-1 microgels counted from TEM images were (467 ± 27), (278 ± 14), and (265 ± 25) nm, respectively. The larger size of Au@PNI-1/2 microgels was attributed to a lower cross-linking density, which was consistent with the results reported previously.^[33,40] Similar results were also observed in SEM images, as shown in Fig. S1 (in electronic supplementary information, ESI). Owing to the large difference in electron density between inorganic nanoparticles and microgels, small Au NPs with diameters of 5 nm to 8 nm could be clearly observed in the enlarged TEM images. These Au NPs were homogeneously embedded in the microgels, as shown in Figs. 1(d)–1(f). The microgels with a higher density of cross-linking points had smaller sizes and were observed to load more Au NPs in terms of mass. It was reasonable because the counter anions around the quaternary ammonium salts at cross-linking points could be exchanged by AuCl₄⁻, and the latter can be reduced to Au NPs. Therefore, the more the cross-linking points, the more the sites to locate AuCl₄⁻, hence leading to more Au NPs. In addition, the hydrophilicity of the microgel allowed the Au NPs loaded therein to be stably dispersed in water for a long time, while independent Au NPs tended to aggregate due to their large surface area (Fig. S2 in ESI).

The Au NPs loaded in the thermo-sensitive microgels were analyzed qualitatively and quantitatively, as shown in Figs. 2 and S3 (in ESI). The UV-Vis spectra in Fig. 2(a) clearly displayed the characteristic plasmonic absorption of Au NPs at 526 nm for Au@PNI-1 microgels, indicating that gold nanoparticle had been successfully introduced into microgels. Meanwhile, TGA and EDS were employed to quantitatively determine the content of Au NPs in the microgels (Fig. S3, in ESI), and the results are listed in Table 1. In TGA, the gold mass content increases from 7.1% (*x* = 0.5) to 17.5% (*x* = 0.67) and 21.3% (*x* = 1), which are in good accordance with the EDS result, *i.e.*, 8.3% (*x* = 0.5), 16.3% (*x* = 0.67), and 22.1% (*x* = 1). From these values, it is concluded that the mass content of Au NPs in the microgels (*C*_{Au}, wt%)

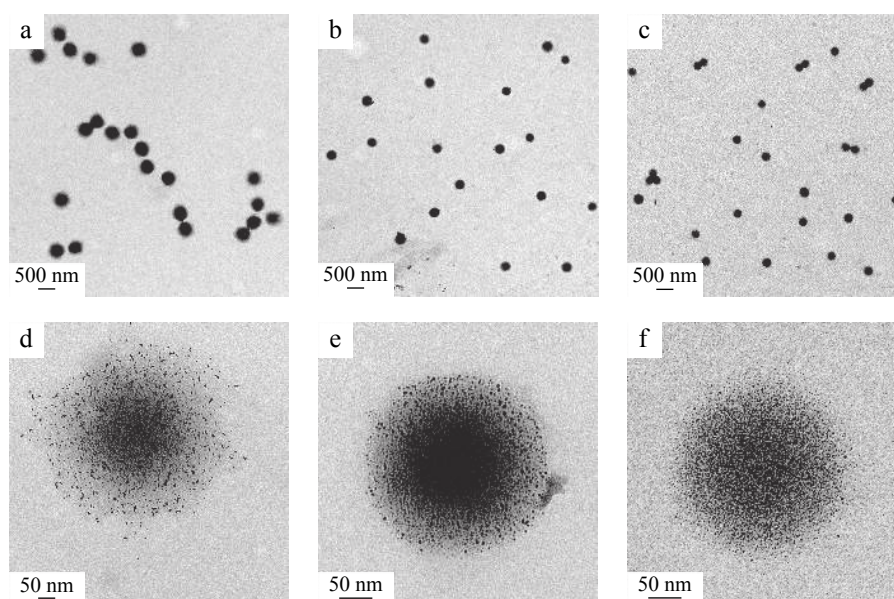


Fig. 1 TEM images of PNI microgel loaded with Au NPs: Au@PNI- x . (a, d) $x = 1/2$, (b, e) $2/3$, and (c, f) $x = 1$. (x : quaternization ratio)

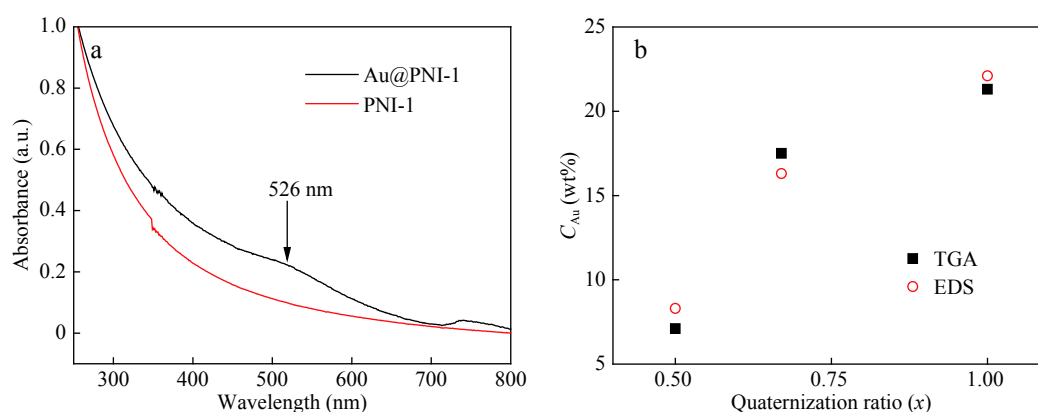


Fig. 2 (a) UV-Vis spectra of PNI-1 microgels before and after loading with Au NPs; (b) The content of Au NPs in the microgels measured by TGA and EDS as a function of quaternization ratio

increased with increasing quaternization ratio (x), as shown in Fig. 2(b). It is reasonable that more quaternary ammonium cations would pair more AuCl_4^- anions, thus produced more gold. That is to say, the content of Au NPs in the microgels could be easily regulated by controlling the quatern-

ization ratio.

The microgels with PNIPAm segments exhibited thermo-sensitive behavior (Fig. 3a), which was expected according to literature.^[30,32,33,40] The thermo-sensitive character, dispersion stability, and swelling properties of the Au@PNI series

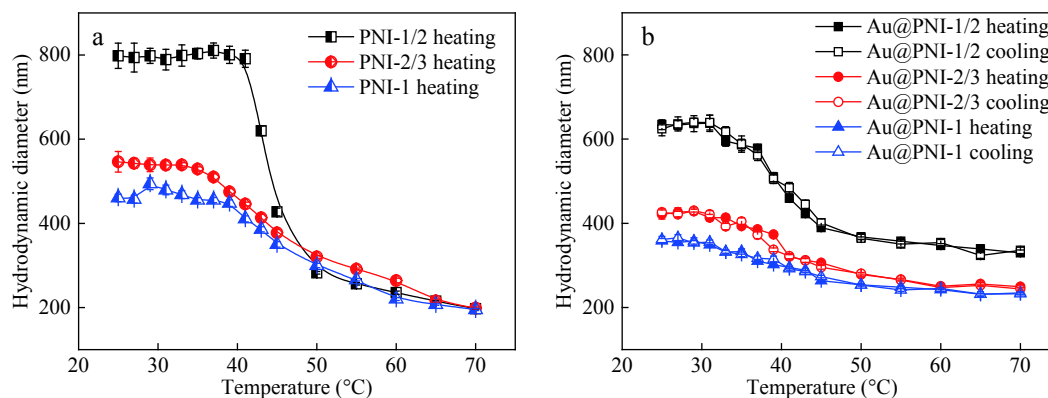


Fig. 3 Hydrodynamic sizes of (a) PNI and (b) Au@PNI microgels measured by DLS as a function of measuring temperature with various quaternization ratios

of microgels were also investigated by DLS before catalytic experiments, as shown in Figs. 3(b), S4 (in ESI) and Table 1. Raising the measuring temperature from 25 °C to 70 °C decreased the hydrodynamic size in all three samples, and a clear phase transition could be observed at 35–45 °C for Au@PNI-1/2 MGs. The volume phase transition temperatures (VPTTs) of Au@PNI microgels were determined to be 39–40 °C (cf. Table 1), by first-order derivative of the plots in Fig. 3(b).^[41] This size contraction was reversible when the measuring temperature went back to 25 °C. It is spotted that the hydrodynamic size was the largest for the sample of the lowest quaternization ratio at temperatures before the phase transition. After the phase transition, all the 3 samples adopted a similar size, as in the collapsed state, the size is determined by their masses that are close to each other. It is not surprising that the hydrodynamic size of Au@PNI-1/2 microgels changed the most obviously against temperature. In comparison with PNI microgels, the nanoreactors had smaller particle sizes and swelling ratios when changing temperature. It was understandable that the negative charges on Au NPs could ionically cross-link the cationic network.^[38,42]

Catalytic Reduction of 4-Nitrophenol with Au@PNI Microgels

The thermo-sensitive Au@PNI MGs were used as temperature-mediated water dispersible catalyst, and their catalytic activities for the reduction of 4-NP were studied.^[43,44] The reaction can be monitored easily and precisely by UV-Vis spectroscopy. The representative UV-Vis kinetic spectra of

4-NP during the reduction are shown in Fig. S5 (in ESI). The decay of adsorption peak at 400 nm indicates the reduction of 4-NP.^[44,45] Note that the PNI microgels without Au NPs imposed zero effect on the reduction of 4-NP, as observed in our control experiment. Due to a large excess of NaBH₄, the reduction rate of 4-NP can be treated as pseudo-first-order rate equation as follows:^[46]

$$\ln \frac{c_t}{c_0} = \ln \frac{A_t}{A_0} = -k_{\text{app}}t = -k_1 S t \quad (1)$$

where c_t and c_0 are the concentration of 4-NP at time t and at initial time of the reaction, respectively; k_{app} is the apparent rate constant; k_1 is the rate constant normalized to S , the surface area of Au NPs normalized to the unit volume of the system.

The value of the apparent rate constant, k_{app} , could be directly obtained by linear fitting the curve of $\ln(C_t/C_0)$ versus time t , as shown in Fig. 4. The catalytic activities of different Au@PNI microgels were investigated first (Fig. 4a). The same amount of Au@PNI microgels (50 μL , $c_{\text{microgel}} = 1.5 \text{ mg}\cdot\text{mL}^{-1}$) was added into the reaction medium and the reaction was performed at 25 °C. The apparent rate constant k_{app} and normalized rate constant k_1 were calculated and listed in Table 2. The microgels immobilized with more Au NPs showed better catalytic effect with the same concentration of microgels. Au@PNI-1 microgels loaded with the smallest Au NPs showed the highest catalytic activity with k_1 of $6.11 \times 10^{-2} \text{ s}^{-1}\cdot\text{m}^{-2}\cdot\text{L}$, which was at a moderate level of

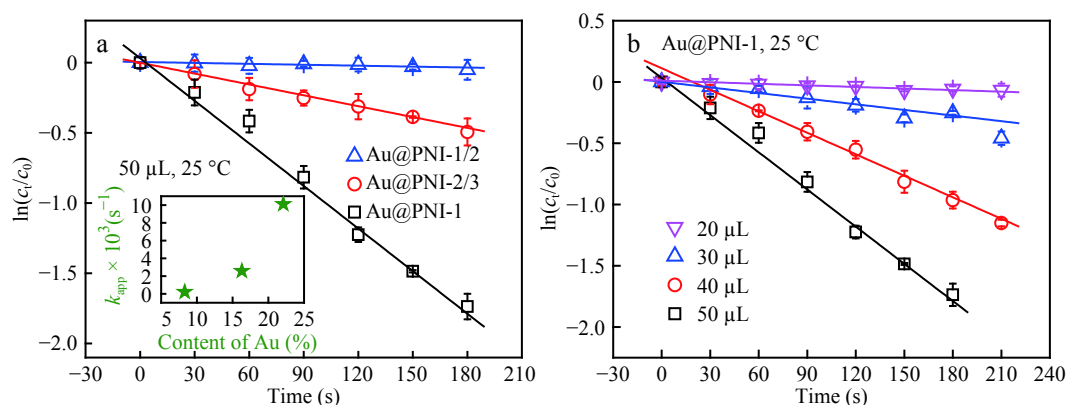


Fig. 4 The linear relationship between $\ln(c_t/c_0)$ and reaction time t for the reduction of 4-NP by adding (a) different Au@PNI microgels and (b) different amounts of Au@PNI-1 microgels, respectively. Inset of (a) is the corresponding plot of k_{app} versus content of gold.

Table 2 Catalytic activity of Au@PNI microgels

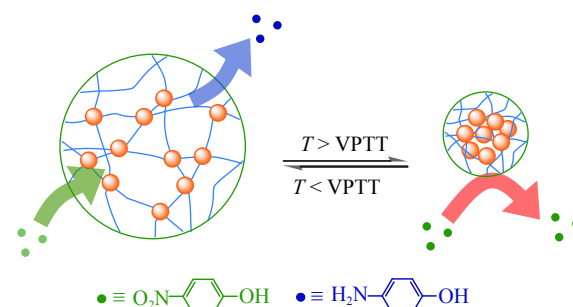
Sample	T (°C)	k_{app} (s^{-1})	k_1 ($\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{L}$)	c^a ($\text{mg}\cdot\text{L}^{-1}$)	d^b (nm)	S ($\text{m}^2\cdot\text{L}^{-1}$)
Au@PNI-1/2	25	4.52×10^{-4}	1.31×10^{-2}	1.8	8	0.034
Au@PNI-2/3	25	2.58×10^{-3}	2.28×10^{-2}	4.4	6	0.113
Au@PNI-1	25	1.01×10^{-2}	6.11×10^{-2}	5.3	5	0.165
Au@PNI-1/2	25	4.30×10^{-3}	1.23×10^{-2}	18	8	0.349
Au@PNI-1/2	30	5.40×10^{-3}	1.55×10^{-2}	18	8	0.349
Au@PNI-1/2	35	6.95×10^{-3}	1.99×10^{-2}	18	8	0.349
Au@PNI-1/2	40	1.24×10^{-3}	3.55×10^{-3}	18	8	0.349
Au@PNI-1/2	45	1.86×10^{-3}	5.32×10^{-3}	18	8	0.349
Au@PNI-1/2	50	1.45×10^{-3}	4.15×10^{-3}	18	8	0.349

^a Total mass concentration of Au NPs in the system; ^b Diameter of the Au NPs

the reported carrier catalytic systems (*cf.* Table S1 in ESI). In addition, Au@PNI-1 microgels were further used to study the effect of the amount of catalyst added to the reduction (Fig. 4b). The results showed that within the range tested here, the more the catalysts existed, the faster the reduction reaction occurred.

As mentioned above, the Au@PNI microgels were thermo-responsive. They swelled well with large cross-linking network in aqueous solution at temperature below VPTTs and collapsed to form dense spheres above VPTTs, as shown in Scheme 2. Since the Au@PNI-1/2 microgels changed the most obviously with temperature, it was employed to study the thermo-sensitivity of the catalytic reaction (*cf.* Fig. 5 and Table 2, 500 μL , $c_{\text{microgel}} = 1.5 \text{ mg} \cdot \text{mL}^{-1}$). The reduction of 4-NP with Au@PNI-1/2 microgels was performed in the range from 25 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$ (Figs. 5a and 5b). The apparent rate constant k_{app} firstly increased with increasing temperature from 25 $^{\circ}\text{C}$ to 35 $^{\circ}\text{C}$.^[47] It was reasonable that the thermo-sensitive Au@PNI-1/2 microgel was hydrophilic and swelled at the temperature below its VPTT, so the reactants could easily diffuse through the swollen cross-linked network to reach the surface of Au NPs in the microgels. Once raising the temperature to 40 $^{\circ}\text{C}$, which is higher than the VPTT of Au@PNI-1/2 microgels, the value of k_{app} decreased dramatically. The reason was that the thermo-

sensitive microgels collapsed to form a dense sphere, which could act as a hydrophobic barrier to prevent the reactants from contacting the Au NPs inside the microgels. With further increasing the temperature, the value of k_{app} increased slightly, which could be explained by Arrhenius equation.^[47] The reaction process which follows Langmuir-Hinshelwood mechanism includes two steps, that is, diffusion and reaction of the reactants on the AuNP surface.^[48] Generally, the latter is the rate-limiting step.^[48] However, in our system, the diffusion and adsorption of the reactants on the AuNP surface were slower when the phase transition of microgels occurred. Similar results were also obtained with palladium and



Scheme 2 The temperature-mediated catalytic activity of Au@PNI microgels

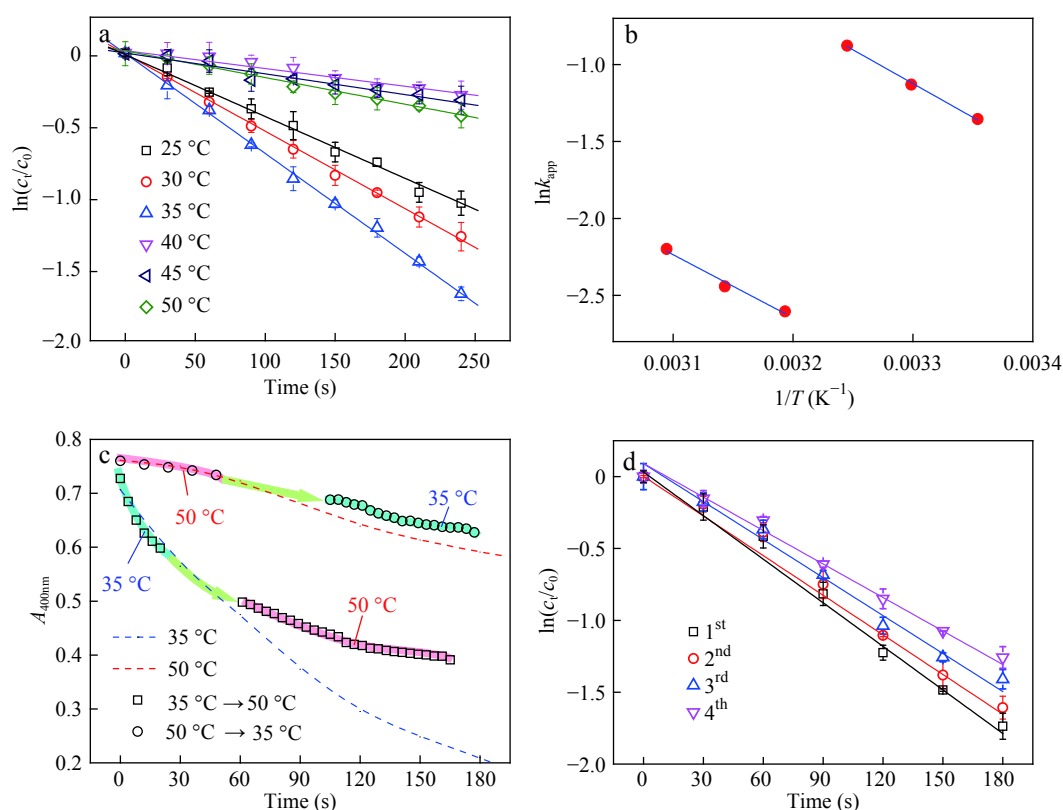


Fig. 5 (a) The linear relationship between $\ln(c/c_0)$ and reaction time t for the reduction of 4-NP with Au@PNI-1/2 microgels at different reaction temperatures; (b) The corresponding plots of the apparent rate constant k_{app} versus reaction temperature; (c) The intensity evolution of UV absorption peak at 400 nm for the reduction at varying temperatures as a function of time; (d) Plots of $\ln(c/c_0)$ versus t for 4-NP reduction at room temperature by recycling use of Au@PNI-1 microgels as the catalyst. The amount of Au@PNI microgels ($c_{\text{microgel}} = 1.5 \text{ mg} \cdot \text{mL}^{-1}$) added were 500 and 50 μL for (a–c) Au@PNI-1/2 and (d) Au@PNI-1, respectively.

silver composite particles.^[37,49] The activation energies, E_a of $\sim 34 \text{ kJ}\cdot\text{mol}^{-1}$ were obtained at the temperature lower or higher than Au@PNI-1/2 microgel's VPTT (Fig. 5b), consistent with the regularity reported by Lu *et al.*^[46] Hence, the activation energy of Au@PNI-1/2 microgels with different architectures was the same, and the difference of catalytic activities was solely ascribed to the diffusional barrier for the reactants.

The reaction temperature was also changed *in situ* to investigate the catalytic activity, as shown in Fig. 5(c). The intensity evolutions of UV absorption at 400 nm ($A_{400\text{nm}}$) were monitored with (increasing) the reaction temperature from 35 °C to 50 °C or the reverse process. The two temperatures selected here are on each side of Au@PNI-1/2 microgel's VPTT, that is, 39 °C. Note that the blue and red solid lines represent the reaction at temperatures of 35 and 50 °C, respectively. The green arrow represents the process of heating or cooling, during which $A_{400\text{nm}}$ was not detected. The dashed lines represent the evolution of $A_{400\text{nm}}$ at the fixed temperature. As increasing the temperature from 35 °C to 50 °C, the reaction rate reduced significantly, while the change of reaction rate was not obvious when lowering the temperature from 50 °C to 35 °C, probably because it takes much more time for the microgels to relax from collapse to swelling in comparison to the opposite process. To sum up, such microgels could be used as catalyst to adjust the reaction rate by simply controlling the temperature.

The recyclability of Au@PNI microgels for the reaction was also studied, which is shown in Fig. 5(d). The Au@PNI-1 microgels could be recycled by centrifugation and reused at least three times with the catalytic activity of $\sim 85\%$. The decrease of activity might be induced by the adsorption of 4-AP on gold surface that quenched the activate sites. Another explanation is that the AuNPs grew to larger sizes after catalyzing 4-NP reduction in the presence of excess NaBH_4 ,^[50] and large particles mostly often have a low activity compared with small ones.^[4]

CONCLUSIONS

A type of spherical microgels with uniform size and small Au NPs embedded in them have been successfully prepared and characterized. The content of Au NPs in microgels could be regulated by controlling the quaternization ratio. The obtained microgels have reversible thermo-sensitive behavior and can catalyze the reduction of 4-nitrophenol in the presence of NaBH_4 . The catalytic activity can be modulated by the thermal phase transition. Such temperature-mediated catalytic system may have promising potential in micro-motors.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2182-7>.

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