

Supporting Information

Thermoresponsive Polymers Based on Poly-vinylpyrrolidone: Applications in Nanoparticle Catalysis

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1. Materials and Methods

PNIPAAm is purchased from Aldrich (MW: 20,000-25,000). THF was dried and distilled under argon and stored with 4 Å molecule sieves. Diisopropylamine was dried and distilled into a dry receiver under argon. N-vinyl-2-pyrrolidone (NVP) was distilled under reduced pressure prior to use. H₂ (99.999 %), RuCl₃·nH₂O (AR grade), AgNO₃ (AR grade) K30 and other chemicals were obtained from commercial sources and used without further purification. All reactions were conducted using Schlenk techniques under argon.

The molecular weight of the polymers was determined by a gel permeation chromatography (GPC) system equipped with a Waters 2410 refractive index detector, a Waters 515 HPLC pump and two Waters styragel columns (HT 3 and HT 4) using THF as eluent at a flow rate of 1 ml/min at 35°C. Data were processed against narrow polystyrenes using Millennium 32 software.

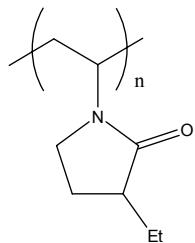
Elemental analyses were performed on an Elementar Vario MICRO CUBE (Germany). NMR spectra were recorded at 20 °C either on a Bruker DMX 400 instrument or a Varian Gemini 300 MHz spectrometer with TMS as internal standard. Temperature-dependent ¹H NMR of C₂-PVP was measured on Bruker DMX 400 instrument in D₂O (3 mg/L). The experiments were started at 20 °C, 25 °C, 30 °C, and 35 °C, respectively. When the machine is heated to desired temperature, the sample was hold inside for another 0.5 h to reach equilibrium. Transmission electron

microscopy (TEM) was carried out on a Philips Tecnai F30 transmission electron microscope operating at 300 keV. TGA data were recorded on a Thermal Analysis SDT2960 simultaneous differential thermal analyzer at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen or air. IR spectra were recorded on a Fourier transform infrared spectrophotometer (Tensor 27, Bruker) with a resolution of 1 cm^{-1} . ESI-MS data were obtained on a Thermo LCQ DECA XP Plus ESI Mass Spectrometer in positive mode. UV-Vis spectra were recorded on a Lambda 35 UV-vis spectrophotometer. XPS spectra were collected on an Axis Ultra spectrometer (Kratos, UK) using monochromatic Al KR (1486.71 eV) radiation at a source power of 225 W (15 mA, 15 kV). Dynamic light scattering (DLS) experiments were conducted on a commercialized spectrometer (Brookhaven Inc, Holtsville, NY) equipped with a BI-200SM Goniometer and a BI-TurboCorr Digital Correlator. A solid-state laser polarized at the vertical direction (GXL-III, 100mW, CNI, Changchun, China) operating at 532 nm was used as the light source.

2. Characterization of C₂-PVP and C₄-PVP

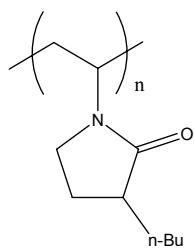
Detailed synthetic procedures and characterization of C₂-PVP, C₄-PVP, as well as other alkyl substituted PVPs, were described in the SI in our previous paper.¹ Therefore only the analytical data for C₂-PVP and C₄-PVP is given here.

Poly-3-ethyl-1-vinyl-2-pyrrolidone (C₂-PVP)



¹H NMR (400MHz, CDCl₃): 0.92 (s, br, 3H), 1.34 (s, br, 2H), 1.54-1.62 (br, 3H), 2.27 (br, 2H), 3.11 (s, br, 2H), 3.76 (br, 1H). IR (KBr, cm⁻¹): 2959, 2933, 2873, 1682, 1492, 1456, 1426, 1377, 1310, 1276, 1132, 809, 798, 769, 718. Anal. Calc. for C₈H₁₃NO: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.86; H, 9.47; N, 9.89. GPC: M_w = 17 k/mol, M_w/M_n = 2.2.

Poly-3-butyl-1-vinyl-2-pyrrolidone (C₄-PVP)



¹H NMR (400MHz, CDCl₃): 0.87 (s, br, 3H), 1.29 (s, br, 6H), 1.60-1.77 (br, 3H), 2.20 (br, 2H), 3.10 (s, br, 2H), 3.70 (br, 1H). IR (KBr, cm⁻¹): 2954, 2929, 2857, 1677, 1491, 1456, 1426, 1376, 1310, 1265, 1136, 1060, 917, 897, 731, 716, 650, 605. Anal. Calc. for C₁₀H₁₇NO: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.73; H, 10.04; N, 8.19. GPC: M_w = 16 k/mol, M_w/M_n = 2.1.

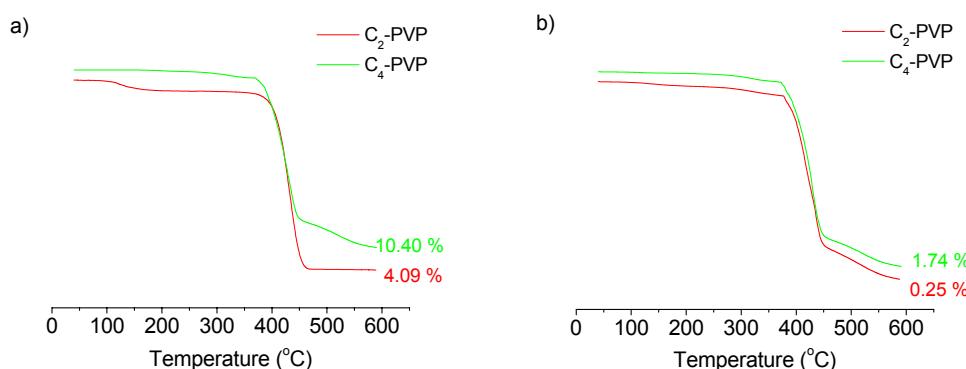


Figure S1. TGA Curves of C₂-PVP and C₄-PVP under (a) nitrogen and (b) air.

Synthesis of C₂-PVP with controlled molecular weight

We synthesized a series of C₂-PVP with different molecular weights by reversible addition fragmentation transfer polymerization (RAFT). The structure of the RAFT agent is showing below. Typically, a mixture of C₂-NVP, RAFT agent, AIBN, and THF as solvent was degassed by three cycles of freeze-vacuum-thaw in glass tubes. Then the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. After 24h, the solution was dropped into a large amount of *n*-hexane, collected by filtration and dried under vacuum overnight to obtain white powders. The molecular weights and M_n/M_w were determined by gel permeation chromatography (GPC) (Fig. S2), and the results were summarized in Table S1

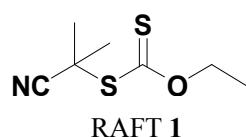


Table S1. Synthesis and GPC analysis of five C₂-PVP with different MW.

Entry	Monomer : RAFT agent ^{a)}	M_n ^{b)}	M_n/M_w ^{b)}	Yield (%)
1	50 : 1	2500	1.21	43
2	100 : 1	3900	1.26	49
3	200 : 1	7900	1.58	59
4	300 : 1	11000	1.52	51
5	600 : 1	16000	1.56	55

a) Polymerization condition: monomer : THF = 1 : 2 (w/w), RAFT agent : AIBN = 10 : 1(mol.), reaction at 60 °C during 24 h; b) Determined by GPC in THF with polystyrene standards; c) Determined by transmittance change during the heating process.

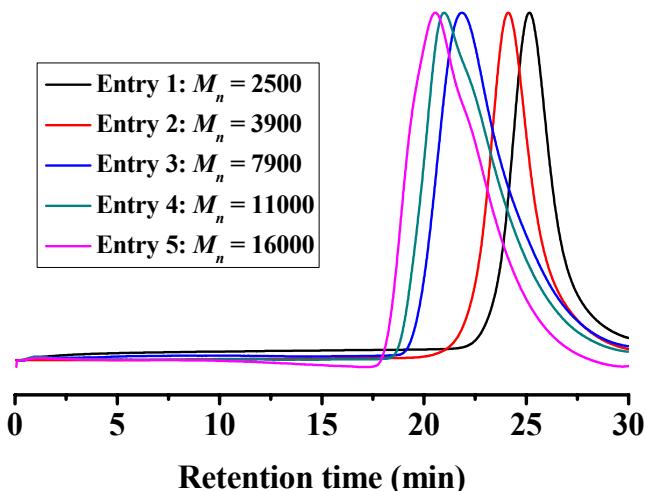


Figure S2. GPC curves of poly(C₂-NVP) with different M_n obtained from RAFT polymerization.

3. LCST/cloud-point and DLS measurement

The LCSTs of all the polymers were determined by measuring transmittance at 500 nm on a Lambda 35 UV-vis spectrophotometer. The samples were heated *in situ* at a speed of 0.1 °C/min. The LCST is defined as the temperature at the initial break point in the resulting transmittance versus the temperature curve.

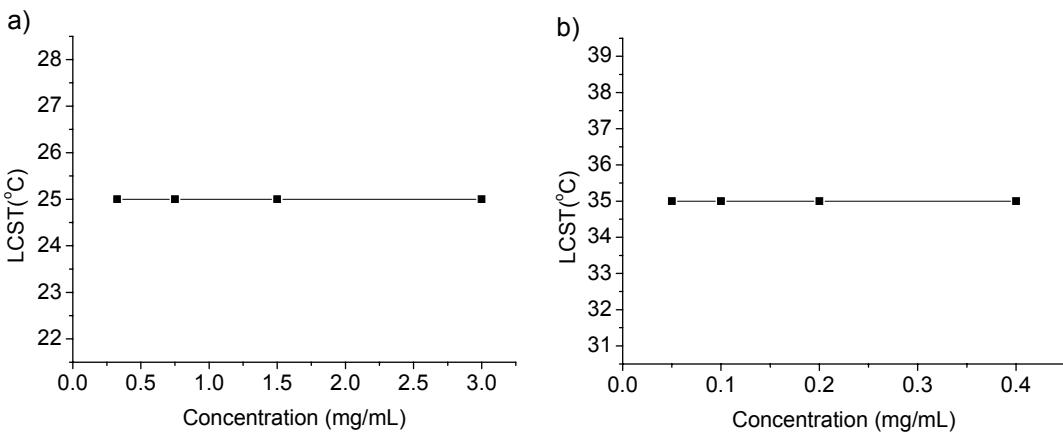


Figure S3. Concentration-LCST relationships of C_2 -PVP (a) and C_4 -PVP (b).

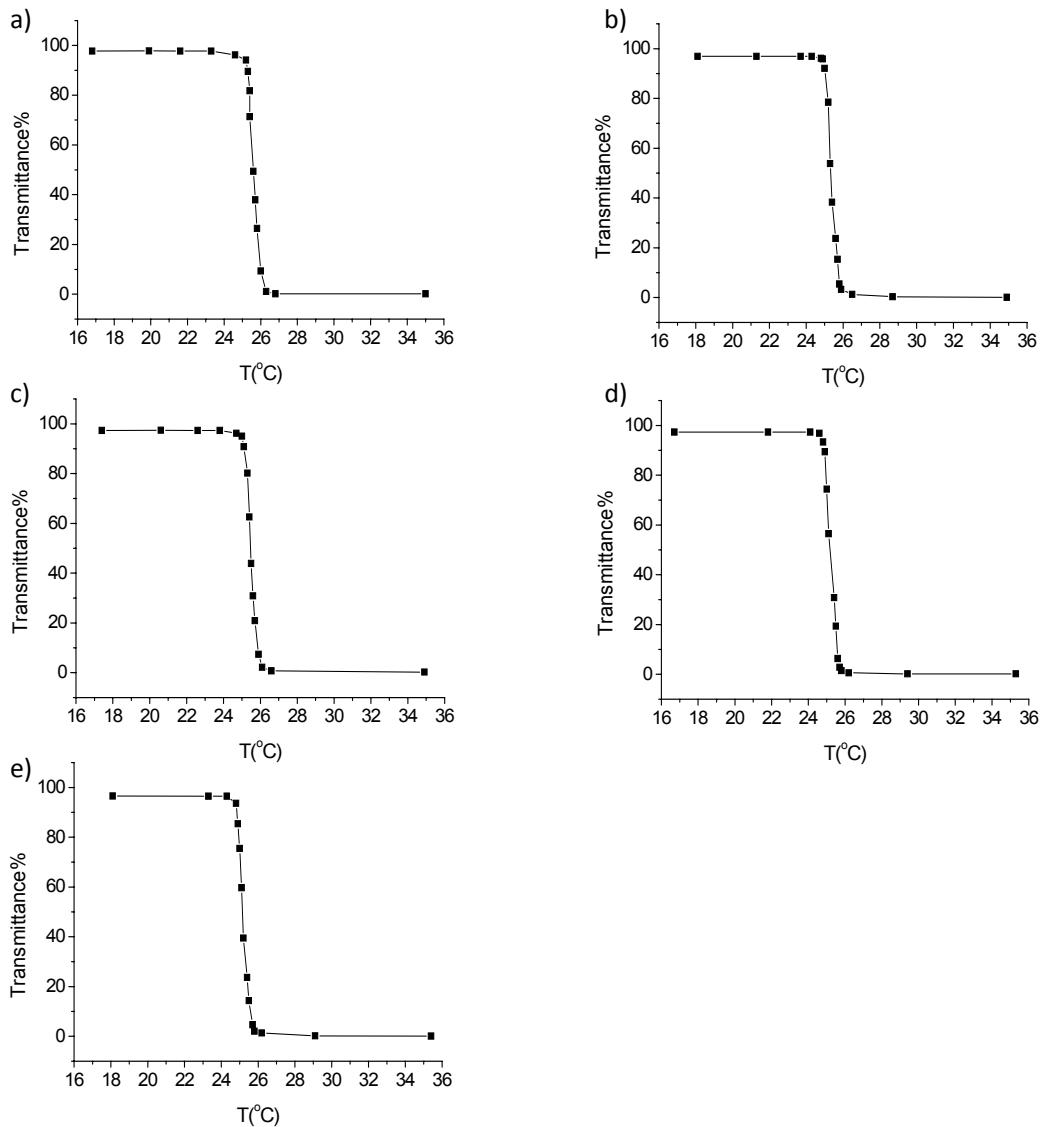


Figure S4. Temperature dependence of light transmittance (500 nm) of the aqueous solutions of C_2 -PVP (3 mg/mL) with different MW. a) $Mn = 2500$, b) $Mn = 3900$, c) $Mn = 7900$, d) $Mn = 11000$, e) $Mn = 16000$.

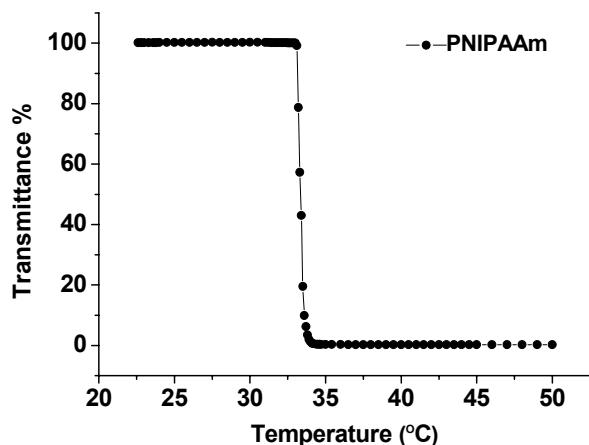
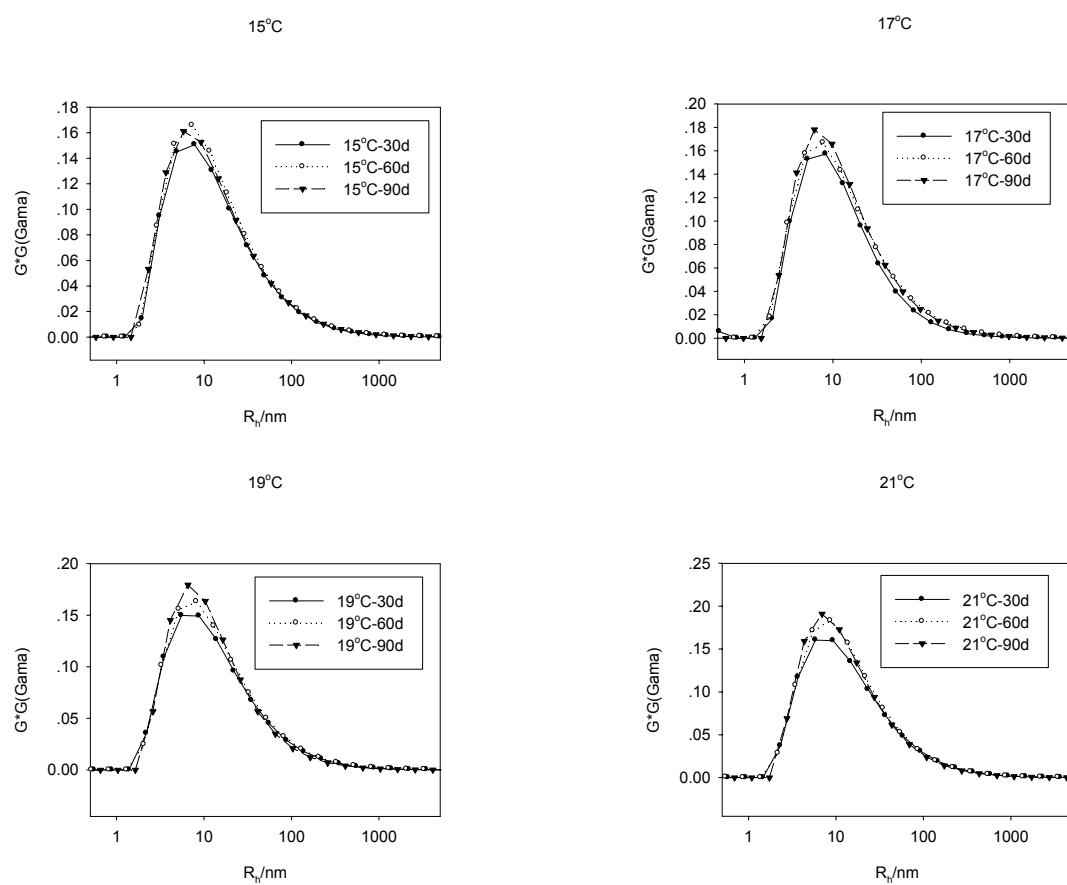


Figure S5. Temperature dependence of light transmittance (500 nm) of the aqueous solutions of PNIPAAm (3 mg/mL).



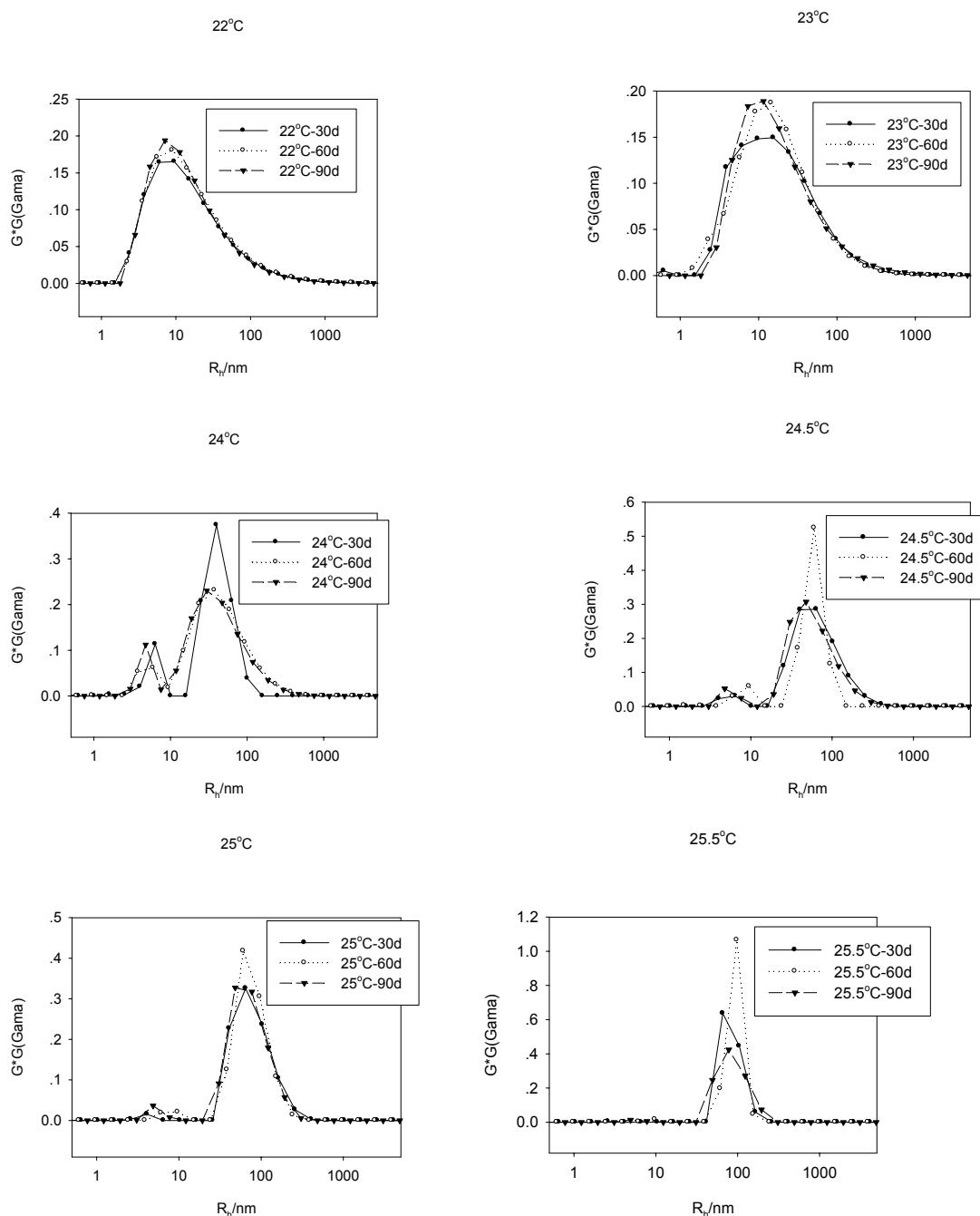


Figure S6. Hydrodynamic radius distributions obtained for C₂-PVP at different temperatures (C₂-PVP = 1 mg/mL).

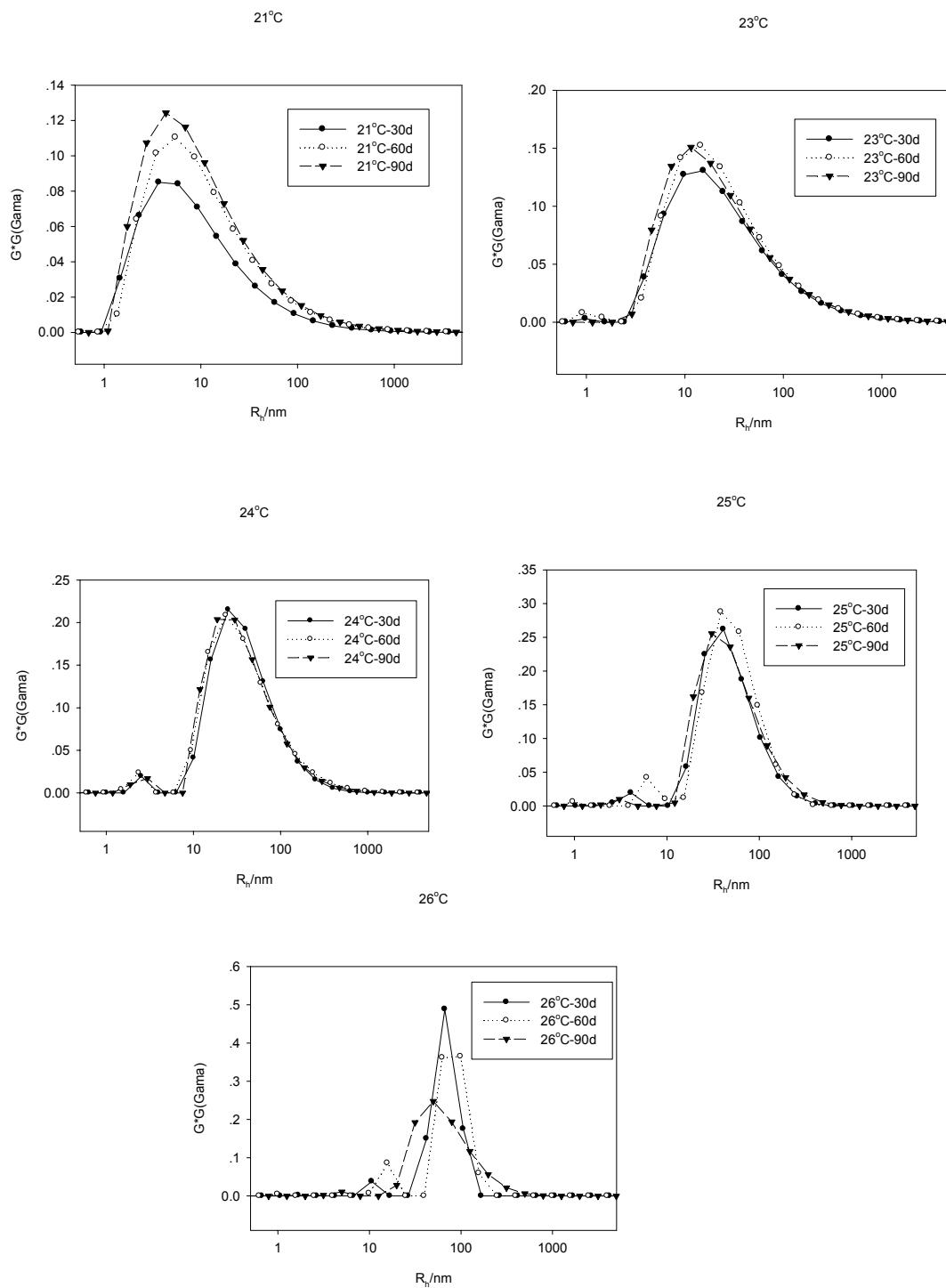


Figure S7. Hydrodynamic radius distributions obtained for C₂-PVP at different temperatures (C₂-PVP = 0.3 mg/mL).

4. Synthesis and characterization of the Au NPs coated with C₂-PVP

HAuCl₄·4H₂O (8.9 mg, 0.0216 mmol) and C₂-PVP (30 mg, 0.216 mmol) were dissolved in water (15 ml) and stirred vigorously. An aqueous solution of NaBH₄ (8.2 mg, 20 wt%, 0.0432 mmol) was then added to the solution in one portion. The color of the solution changed immediately from orange to brown and effervescence was observed. The stirring was stopped when no effervescence was observed. The Au NPs were formed quantitatively, as indicated by the complete disappearance of the absorption band of AuCl₄⁻ at 293 nm (see Figure S8). The brown solution of Au NPs can be stored under ambient conditions for months without the formation of precipitates.

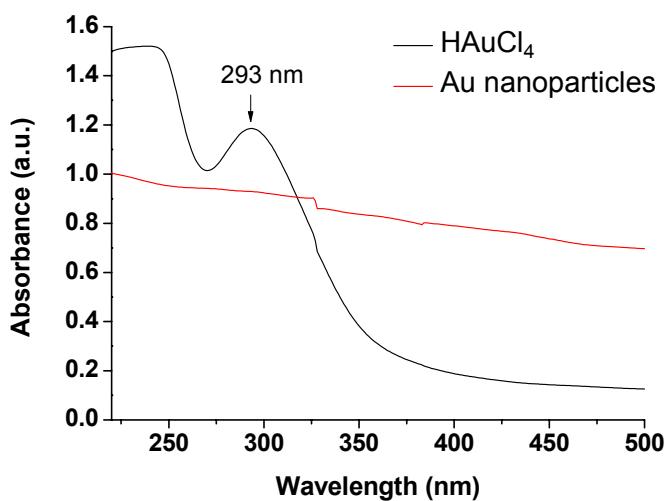
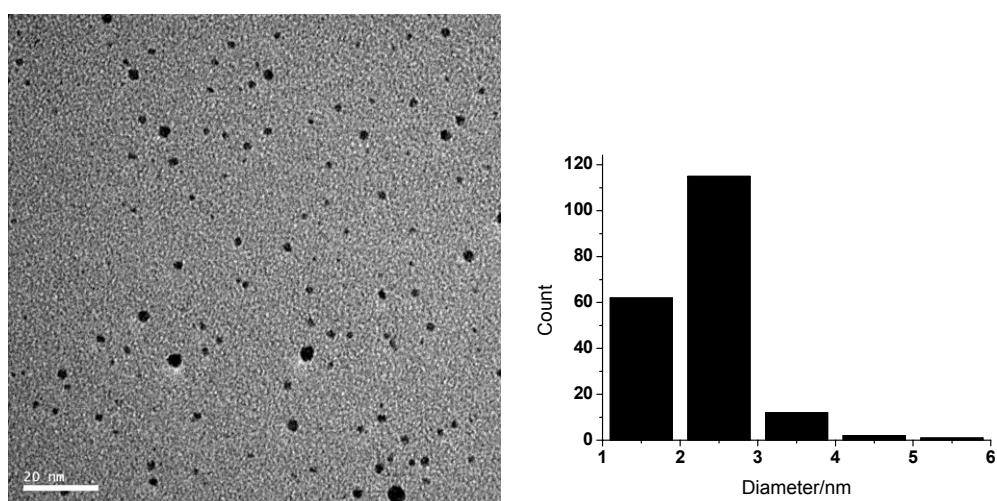


Figure S8. Comparison of UV spectrum before (dark) and after (red) NaBH₄ reduction.

For TEM analysis, the Au NPs water solution (1 mL) was treated by ultrasonication for 1 h, and then one drop of the solution was placed on a copper grid coated with a polymer or carbon film. The TEM measurements were carried out on a Philips Tecnai F30 transmission electron microscope operating at 300 keV. The size distributions of Au NPs were determined from ~150 particles.

a)



b)

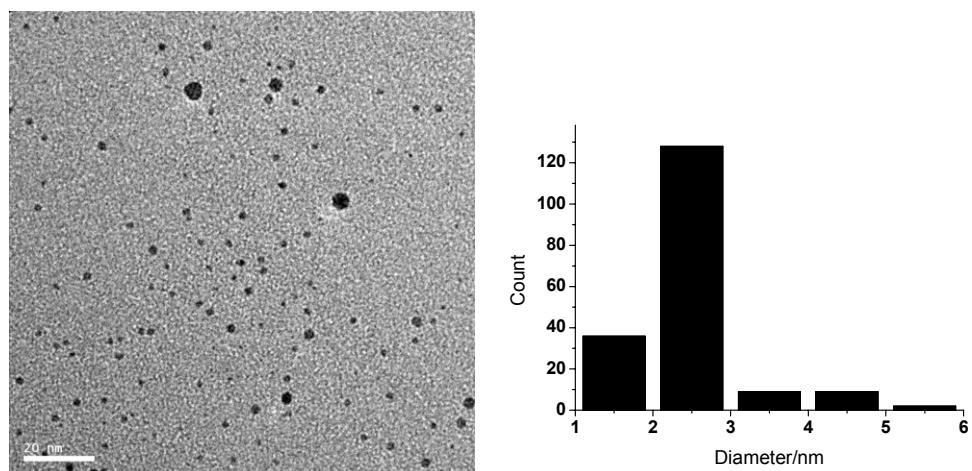


Figure S9. TEM micrographs and size distributions of Au NPs. (a) Before catalysis, $d = 2.2 \pm 0.5$ nm, and (b) after catalysis, $d = 2.4 \pm 0.5$ nm.

Stability of Au NPs under different pH and ionic strength.

Standard pH solutions were prepared as described below:

pH = 2.6: 0.75 ml 0.2 M NaAc mixed with 9.25 ml 0.3 M HAc

pH = 5.0: 7ml 0.2 M NaAc mixed with 3 ml 0.3 M HAc

pH = 9.2: 1 ml 0.1 M Na₂CO₃ mixed with 9 ml 0.1 M NaHCO₃

pH = 10.8: 9 ml 0.1 M Na₂CO₃ mixed with 1 ml 0.1 M NaHCO₃

All pH values were measured by a pH meter.

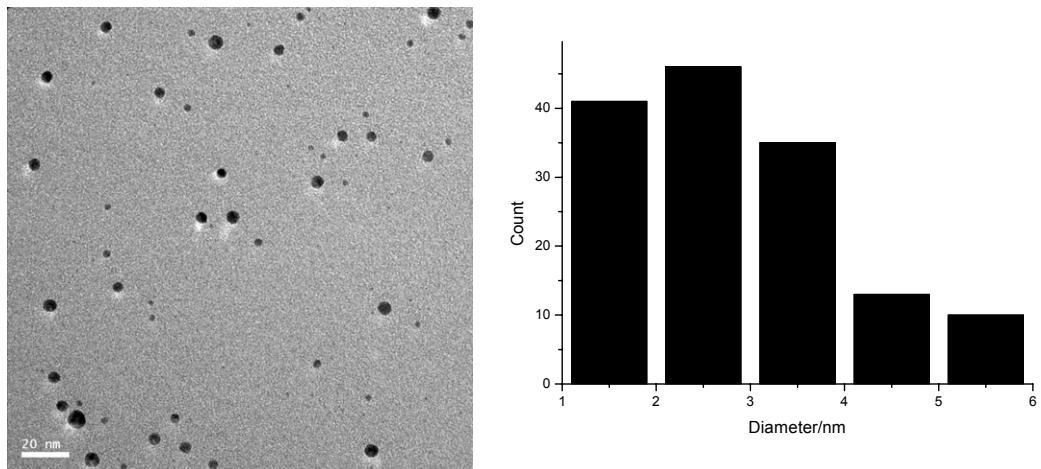
The resulting Au NPs were kept under different pH (2.6, 5.0, 6.7, 9.2, 10.8, respectively) and ionic strength (saline solution, 24 wt%, 12 wt%, 6 wt%, 3 wt%, respectively) for one week, see Figure S10. The Au NPs are quite stable under different pH, remaining homogenous, clear solutions in water. They are also tolerant with salt; however, the colloidal was unstable in very concentrated saline solution (sample 6).

Some samples (1, 5, 7, 9) were also tested by TEM analysis, which revealed that under different pH, the size of Au NPs remains relatively constant (sample 1 and 5, Figure S11, a-b) whereas in the presence of high ionic strength, the size of Au NPs increased (sample 7 and 9, Figure S11, c-d).

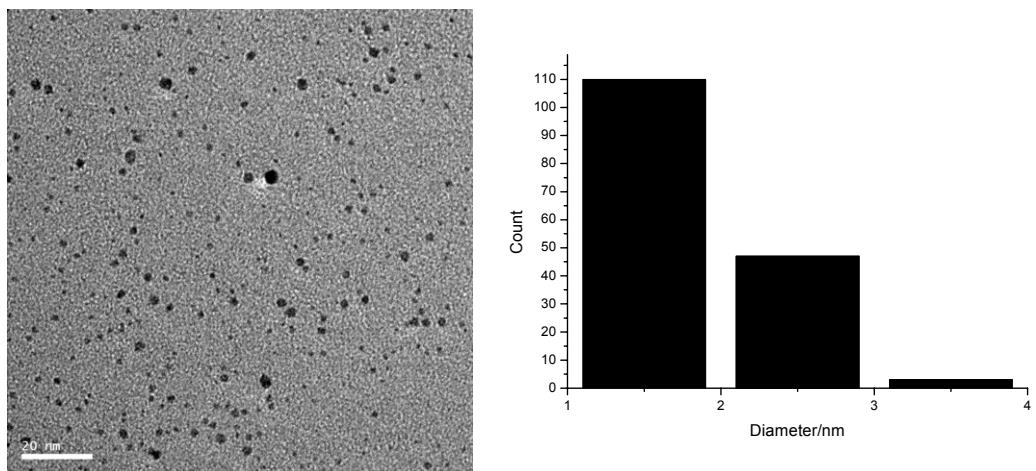


Figure S10. Pictures of Au NPs kept under different pH and ionic strength after one week (from 1 to 9: pH = 2.6 (NaAc/HAc), pH = 5.0 (NaAc/HAc), pH = 6.7 (H₂O), pH = 9.2 (Na₂CO₃/NaHCO₃), pH = 10.8 (Na₂CO₃/NaHCO₃), 24 wt% NaCl in H₂O, 12 wt% NaCl in H₂O, 6 wt% NaCl in H₂O, 3 wt% NaCl in H₂O).

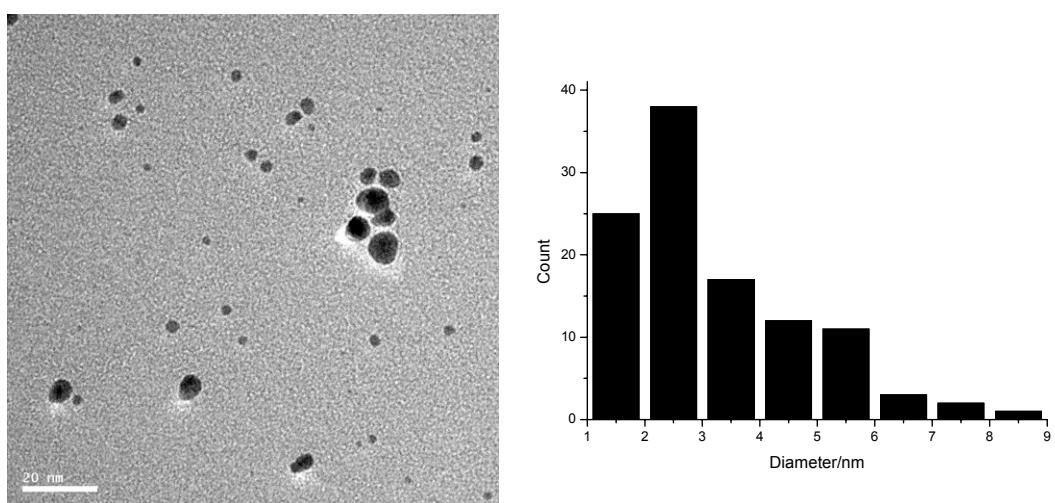
a)



b)



c)



d)

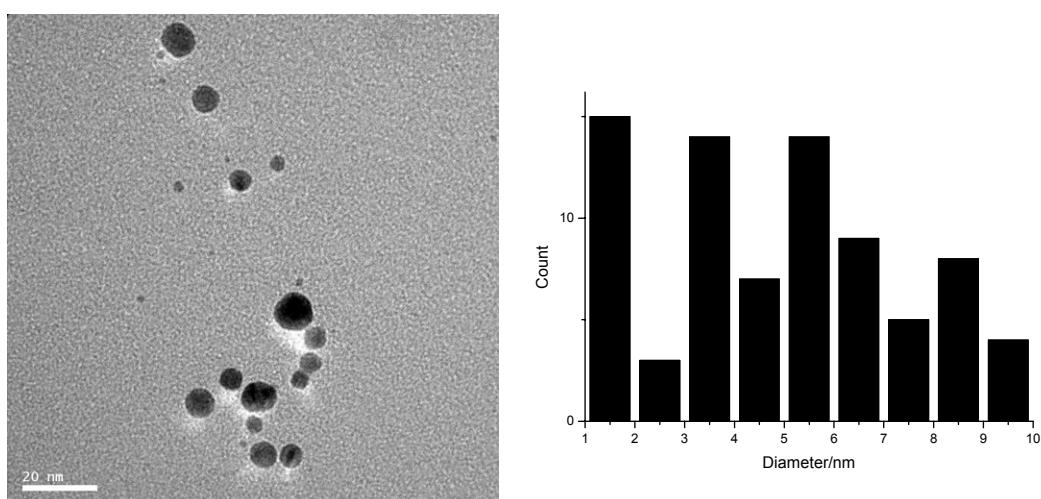


Figure S11. TEM micrographs and size distributions of Au NPs after keeping under different conditions for 1 week. a) pH = 2.6, size = 2.9 ± 1 nm, b) pH = 10.8, size = 2.0 ± 0.4 nm c) 12 wt% NaCl in water, size = 3.2 ± 1.5 nm, d) 3 wt% NaCl in water, size = 4.9 ± 2.5 nm.

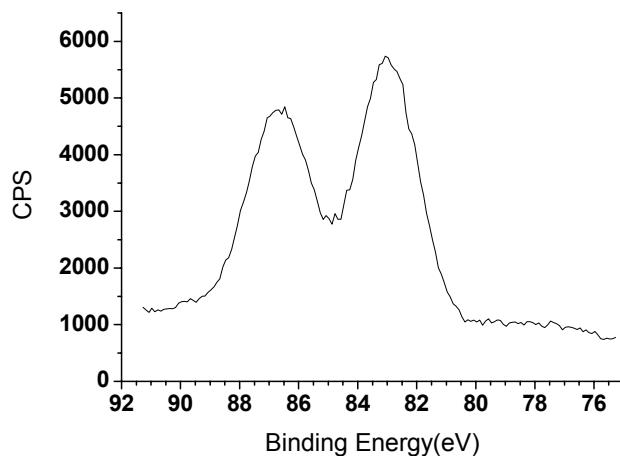


Figure S12. XPS data of Au NPs (left peak is corresponded to Au $4f_{5/2}$ and right peak corresponded to Au $4f_{7/2}$).

Compared to bulk gold, whose binding energy (BEs) for $4f_{7/2}$ is 84.0 eV, the BEs of Au NPs protected by C₂-PVP is significantly smaller, indicating negative charge states of Au NPs. This observation was in accordance with previous studies on Au NPs-PVP,² suggesting the interaction between C₂-PVP and Au NPs is similar to that of PVP.

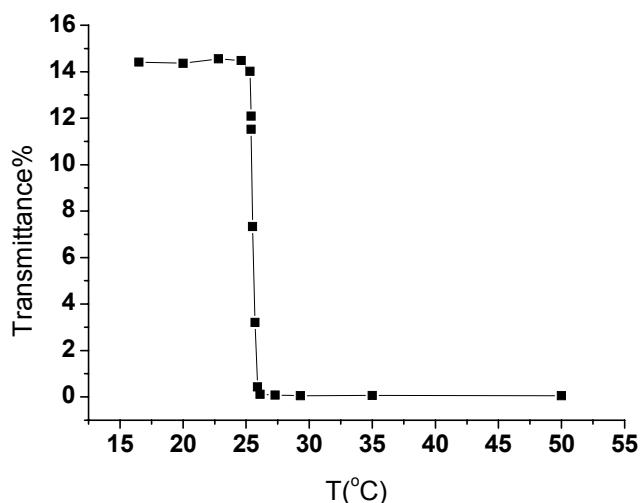


Figure S13. Temperature dependence of light transmittance (500 nm) of the aqueous solutions of Au NPs (1.73 mM) capped by C₂-PVP (17.3 mM).

LCST of Au NPs capped by C₂-PVP was determined the same way as described for pure C₂-PVP in water (see Figure S13).

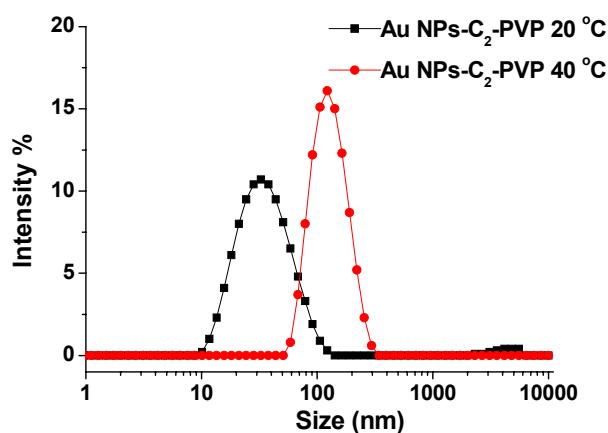


Figure S14. DLS measurement of Au NPs-C₂-PVP at different temperatures (C₂-PVP: 0.2 mg/mL, C₂-PVP:Au = 10:1).

The TGA curves of C₂-PVP in the presence of Au NPs (see Figure S14) were considerably different from pure C₂-PVP. The decomposition temperature shifted from about 360 °C for pure C₂-PVP to about 300 °C for Au NPs-C₂-PVP, indicating that Au NPs can accelerate the decomposition of polymers. Another difference is that the weight percentage of residue of Au

NPs-C₂-PVP is about 60 % and 35 % in nitrogen and air atmosphere respectively, which is much higher than the case of pure C₂-PVP. This difference is partly due to Au NPs, which account for 12 wt% of the sample, are inert upon heating. Other effects, such as adsorption ability of Au NPs, may also be responsible for the weight increase of the residue.

a)

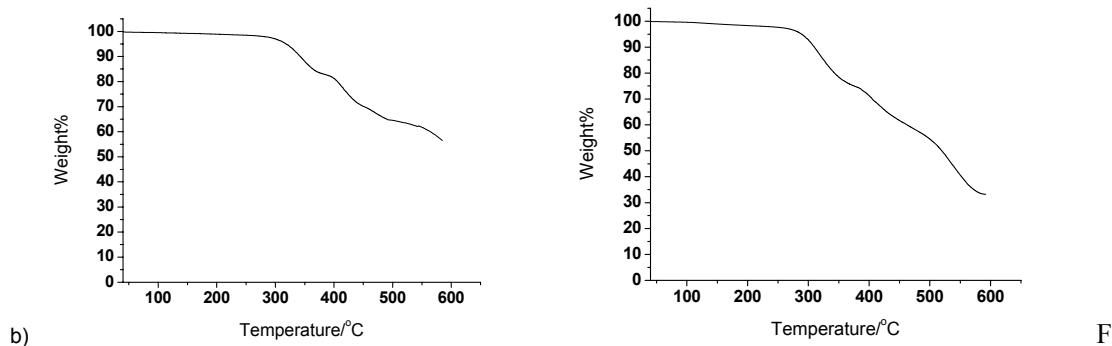


Figure S15. TGA Curves of Au NPs-C₂-PVP under (a) nitrogen and (b) air.

5. Au NP-C₂-PVP catalyzed reduction of 4-nitrophenol by NaBH₄

An aqueous solution containing Au-C₂-PVP ($C_{Au} = 0.04$ mmol/L, C₂-PVP/Au = 10/1, 1.5 mL)³ and 4-nitrophenol (0.20 mmol/L) was transferred into a standard quartz cell. The cell was heated/cooled in situ to the desired temperature. After addition of a preheated aqueous solution of NaBH₄ (10 mmol/L, 1.0 ml), spectra were recorded on a Lambda 35 UV-vis spectrophotometer. In total four temperatures, i.e. 15, 20, 25 and 30 °C, were selected for the determination of the reaction kinetics.

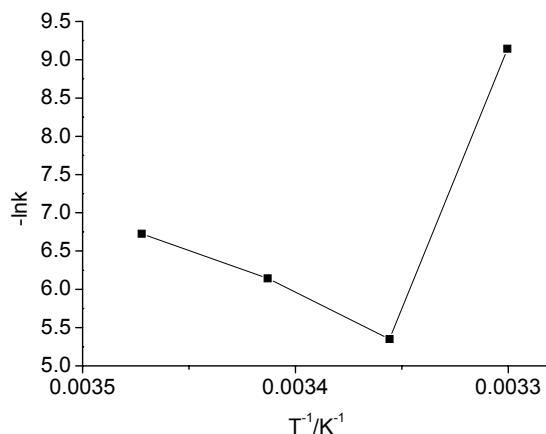


Figure S16. Arrhenius plot of the reaction rate k .

¹ N. Yan, J. G. Zhang, Y. Y. Tong, S. Y. Yao, C. X. Xiao, Z. C. Li, Y. Kou, *Chem. Commun.* **2009**, 4423.

² H. Tsunoyama, N. Ichikuni, H. Sakurai, T. Tsukuda, *J. Am. Chem. Soc.* **2009**, *131*, 7086.

³ It is noteworthy that it is possible that not all C₂-PVP are capped on the Au NPs surface. However, the ratio of C₂-PVP and Au NPs remains constant since both capping agent and Au NPs are homogenously dispersed in the solution.