Electronic Supplementary Information for

Graphene-based smart catalytic system with superior catalytic performances and temperature responsive catalytic behaviors

Junjie Qi[a], Weipeng Lv [a,b], Guanghui Zhang[a], Yang Li[a], Guoliang Zhang[a], Fengbao Zhang[a] and Xiaobin Fan*[a]

School of Chemical Engineering & Technology, Tianjin University, Tianjin, China. 300072.

E-mail: xiaobinfan@tju.edu.cn

Experiment sections

Synthesis of smart G–Au@Pt hybrids

1 mL of an aqueous 10 mM $HAuCl_4$ solution was added to GO suspension (30 mL, 0.033 mg/mL) at boiling point (= reaction temperature for all NP preparation steps) under vigorous magnetic stirring, then the mixture was reduced by citrate solution (3.5 mL, 10 mM). After 0.5 h, silver nitrate solution (1 mL, 10 mM) was added to the stirred solution dropwise, and, subsequently citrate solution (2 mL, 10 mM) was added. After 1 hour, K_2PtCl_6 solution (1 mL, 10 mM) was added and a dark mauve colloid was obtained 3 h later. After cooling down to room temperature, the product was centrifuged and washed with water several times and the finally concentration was 1 mg/mL. DexPNI–SH was synthesized by a RAFT polymerization process as our previous reports.[1, 2] DexPNI–SH (50 mg) was mixed with G–Au@Pt hybrid (10 mL, 1 mg/mL) by sonication at 10 °C for 30 min, then removed redundant polymer which unconnected with G–Au@Pt hybrid by times centrifuged.

Reduction of 4-nitrophenol catalyzed by smart G–Au@Pt hybrids

To avoid the delay caused by the competitive and prior reaction between the dissolved oxygen and $NaBH_4$, in the standard quartz cuvette with a 1 cm path length, $NaBH_4$ (2.5 mL, 10 mM) and 4-nitrophenol (250 μL, 1 mM) solution were first taken at different temperatures. Then, DexPNI–SH-*f*-G–Au@Pt hybrids (250 μL, 3.3 mg/mL) was added to this solution. Immediately after the addition of smart G–Au@Pt hybrids, UV spectra of the mixture were recorded with a UV-vis spectrometer. Note that, about 3 seconds delay is neglected for the necessary response time of UV-vis spectrum measurements. The kinetic study of the reaction was performed by measuring the change in intensity of the absorbance at 400 nm with time. The spectra were recorded every 0.5 minutes. Control experiments showed that no reduction occurred without smart G–Au@Pt hybrids. And G–Au@Pt, DexPNI–SH-*f*-G–Au hybrids, DexPNI–SH-*f*-G–Pt hybrids and DexPNI–SH-*f*-G–Au and G–Pt mixture as catalyst has performance at same concentration at 25 °C.

Characterizations：

The G-Au@Pt and smart G-Au@Pt hybrids were characterized by high resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20), scanning electron microscope (SEM) (Hitachi S-4800), X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer, PHI 1600 spectrometer), and Raman spectroscopy (NTEGRA Spectra). UV-vis absorbance spectra were taken on a Unico 2802 UV-vis spectrometer with temperature controller, which is a circulating water baths linked to the equipment, and the solutions were allowed to stand for 15 min at each desired constant temperature.

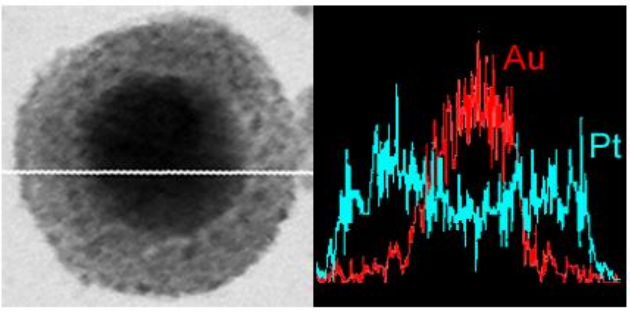

Figure S1. STEM-EDX of line scanning of G–Au@Pt.

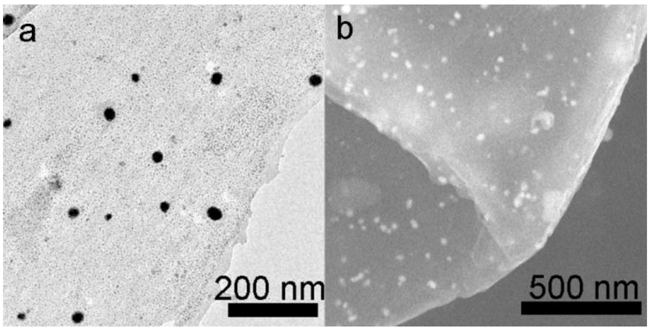

Figure S2. (a) TEM and (b) SEM image of DexPNI–SH-*f*-G–Au@Pt hybrids.

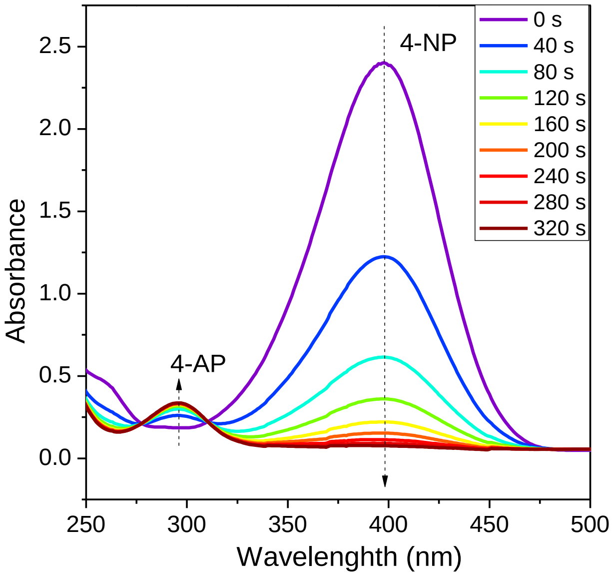

Figure S3. The evolution of the UV-vis spectra of 4-NP reduction in the presence of DexPNI–SH-*f*-G–Au@Pt at 25 °C.

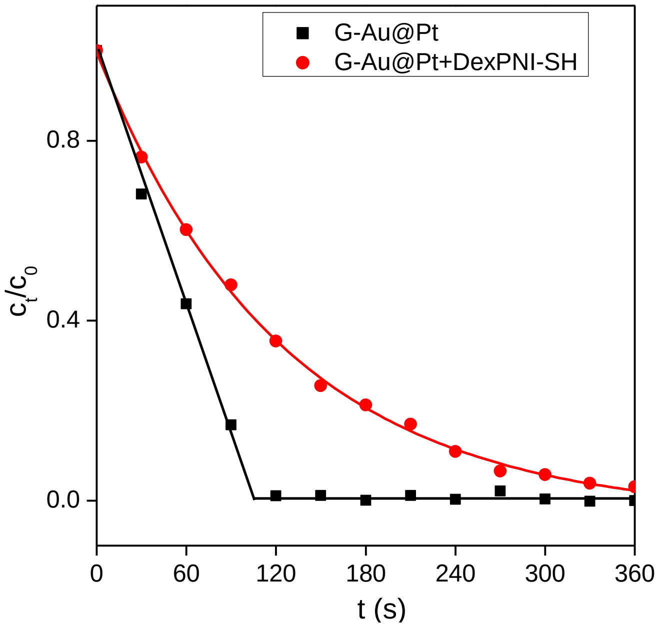

Figure S4. The reaction activity of G–Au@Pt and DexPNI–SH-*f*-G–Au@Pt in the reduction of 4-NP. The G–Au@Pt shows better catalytic performance, as the complete reaction was achieved within about 120 s. In addition, the reduction is a zero-order reaction, while a pseudo-first-order reaction was observed for DexPNI–SH-*f*-G–Au@Pt as catalyst. The kinetic data of polymer functionalization noble metal as catalyst were fitted by a first-order rate law in many works.[3-5] Two main reasons may account for these differences. The first one is the increased diffusion resistance caused by the DexPNI polymer. The second one is thiol-end group "poision" the catalytic site of noble metal. However, the DexPNI–SH-*f*-G–Au@Pt system still shows decent catalytic activities with tunable catalytic activities. This means only limited catalytically active sites of the supported Au@Pt nanoparticles were covered by the thiol-end groups. For our system, due to the high catalytic activities of the supported Au@Pt nanoparticles and the diffusion resistance caused by the outer DexPNI–SH polymer layer, the reaction became mass transfer controlled, and a pseudo-first-order reaction was clearly observed. In fact, that is the main mechanism to control the catalytic activities of the DexPNI–SH-*f*-G–Au@Pt.

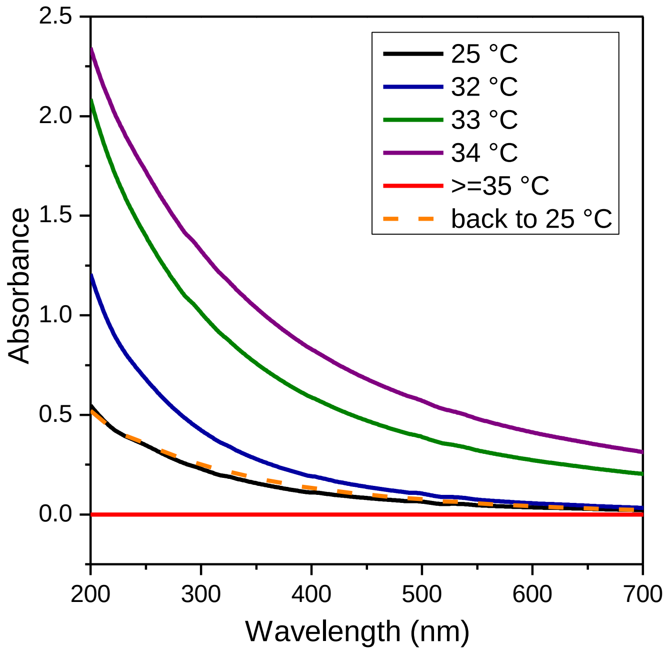

Fig S5 The temperature-dependent optical transmittance curve of DexPNI–SH-*f*-G–Au@Pt vs time.

The temperature-dependent optical transmittance of DexPNI–SH-*f*-G–Au@Pt are greatly dependent on PNIPAAm chain length of copolymer and polymer concentration. Generally speaking, the longer PNIPAAm chain length and the higher polymer concentration, the lower LCSTs and the sharper phase transitions of the copolymer. In our experiment, the PNIPAAm chain length of copolymer is 36 and polymer concentration is 5 mg/mL, thus the cloud points (50% Transmittance) of DexPNI–SH-*f*-G–Au@Pt is about 32 °C with a quite sharp thermal phase transition behaviors.[1]

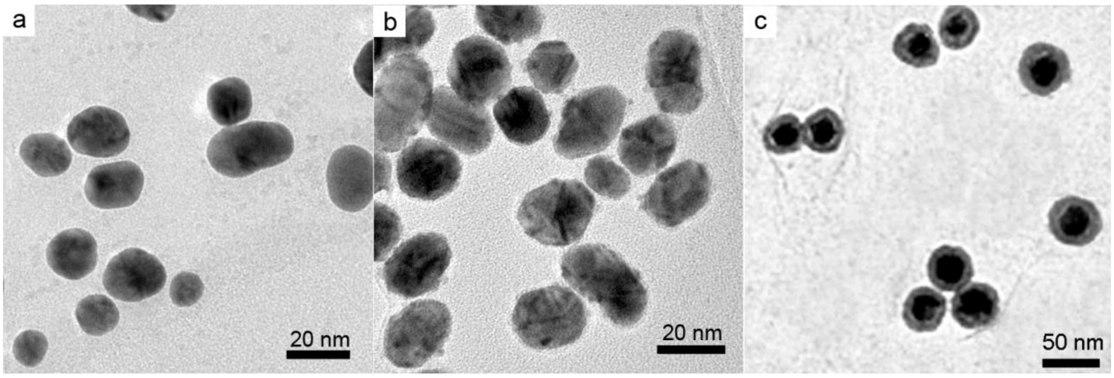

Fig S6 TEM images of (a) G–Au, (b)G–Pt and (c)G–Au@Pt.

The volume of a single metal nanoparticle is $v = \frac{4}{3}\pi r^3$(r is the radius of the metal nanoparticle). The amount of metal nanoparticles is $N = \frac{V_{\text{total}}}{v} = \frac{V_{\text{total}}}{\frac{4}{3}\pi r^3}$. The superficial area of a metal nanoparticle $s = 4\pi r^2$. Therefore, the total specific surface area of the nanoparticles is $S_{\text{total}} = 4N\pi r^2 = \frac{3V_{\text{total}}}{r}$. Considering the density and molecular weight of Au and Pt are approximately equal and all the amount of metal precursor is constant, the total volume (V_{total}) of the nanoparticles is approximately equal. Therefore, the total specific surface area S_{total} is in inverse proportion to the radius of the single metal nanoparticle r. As shown in Fig S6, r_{Au}≈10 nm、r_{Pt}≈13 nm、$r_{\text{Au@Pt}}$≈20 nm, so $S_{\text{Au}}>S_{\text{Pt}}>S_{\text{Au@Pt}}$. Although the nanoparticles constituted by the individual counterparts (Au nanoparticles or Pt nanoparticles) have larger S_{total}, they displayed less catalytic activities. That is to say, the superior catalytic activity of the supported Au@Pt should be attributed to the synergistic catalytic effect arising from the unique core-shell structure.

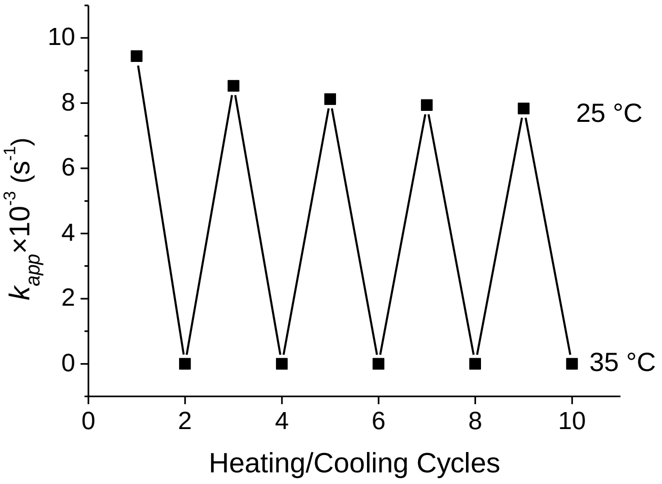

Fig S7 k_{app} of 4-NP reduction as a function of the heating/cooling cycles between 35 and 25 °C

1. W. Lv, S. Liu, W. Feng, J. Qi, G. Zhang, F. Zhang and X. Fan, *Macromolecular Rapid Communications*, 2011, **32**, 1101-1107.
2. W. Lv, S. Liu, X. Fan, S. Wang, G. Zhang and F. Zhang, *Macromol. Rapid Commun.*, 2010, **31**, 454-458.
3. Y. Mei, Y. Lu, F. Polzer, M. Ballauff and M. Drechsler, *Chem. Mater.*, 2007, **19**, 1062-1069.
4. D. Y. Zhao, X. Chen, Y. Liu, C. L. Wu, R. J. Ma, Y. L. An and L. Q. Shi, *J. Colloid Interface Sci.*, 2009, **331**, 104-112.
5. Y. Lu, Y. Mei, M. Drechsler and M. Ballauff, *Angewandte Chemie International Edition*, 2006, **45**, 813-816.