Supporting Information

Responsive hybrid nanosheets of hyperbranched poly(ether amine) as 2D-platform for metal nanoparticles

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1. Experimental Section

Materials: POSS/AN-ended hyperbranched poly(ether amine) (**HPA**) was synthesized in our lab according to previous report,¹ while the mole ratio of POSS and AN moieties in **HPA** is 1/1. Tetrachloroauric(III) acid (HAuCl₄, Sinopharm Chemical Reagent), Silver nitrate (AgNO₃, Sinopharm Chemical Reagent), p-nitrophenol (Nip, Sinopharm Chemical Reagent), sodium borohydride (NaBH₄, Sinopharm Chemical Reagent) were all used without further purification. Other chemicals are of analytical grade except as noted.

Methods: The UV-visible spectra of the sample were checked by a UV-2550 spectrophotometer (Shimadzu, Japan). The fluorescence emission spectra of the sample were recorded under QM/TM/IM steady-state & time-resolved fluorescence spectrofluorometer (PTI Company, USA). The excitation wavelength was set at 381 nm, and the fluorescence emission spectra were recorded between 400 and 650 nm. The data were all normalized. The DLS measurements were performed using a ZS90 Zetasizer Nano ZS instrument (Malvern Instruments Ltd., U.K.) equipped with a multi- τ digital time correlation and a 4 mW He-Ne laser (λ = 633 nm) at an angle of 90 °C. Regularized Laplace inversion (CONTIN algorithm) was applied to analyze the obtained autocorrelation functions. The pH values of the samples were tuned by 0.3%

phosphate-citric acid buffer solution. All the samples were equilibrated at the desired temperature for 2 min before measurement. The TEM images were obtained using a JEM-2100 (JEOL Ltd. Japan) transmission electron microscope operated at an acceleration voltage of 200 kV. The sample was prepared by dropping the nanosheets solution onto copper grids coated with a thin polymer film, and then dried at 30 °C for 24h. No staining treatment was performed for the measurement. The AFM images were obtained by using a scanning probe microscope (SII Nanonavi E-sweep, Japan) operated in the tapping mode by using silicon nitride cantilevers with a force constant of 0.12 N/m. The samples were prepared by dropping dilute nanosheets solution on a mica sheet and then dried at 30 °C for 24 h.

Preparation of HPA nanosheets (hPEA-NSs) Decorated with Gold Nanoparticles (AuNP@ hPEA-NSs) and Silver Nanoparticles (AgNP@ hPEA-NSs): To 3 mL hPEA-NSs solution (1 g/L), 0.1 mL HAuCl₄ aqueous solution (5 g/L) was added, then the ratio of HAuCl₄ and the polymer nanosheets is about 1:6 (w/w). The mixture was equilibrated at room temperature (about 20 °C) for 2 h to make AuCl₄⁻ adsorbed onto the hPEA-NSs by electrostatic interactions, and then the mixture was heated to 40 °C and equilibrated for 3 h to form gold nanoparticles (AuNPs) through reduction reaction of HAuCl₄ by amino groups, and then hPEA-NSs decorated with AuNPs were obtained. hPEA-NSs decorated with different amounts of AuNPs were prepared similarly, while HAuCl₄ and the polymer nanosheets in feed was 1:24, 1:18, 1:12, 1:8, 1:6, and 1:4 (w/w), respectively. AgNP@hPEA-NSs were obtained similarly except for reduction at 40 °C for 12 days.

Catalytic experiment of AgNP@hPEA-NSs: At room temperature (25 °C), 0.75 mL of NaBH₄ solution (40 mmol/L) was added into 2 mL of Nip solution (0.15 mmol/L) that was contained in a glass cuvette. Then, 0.25 mL of AgNP@hPEA-NSs solution ([Ag] = 9.8×10^{-4} mol/L) was added, and UV-vis spectra of the sample were taken every 2 min in the range of 250-550 nm. The rate constant of the reaction was determined by measuring the change of the intensity at 400 nm with time.

Results and Figures



Figure S1. The UV-vis spectra of AuNP@hPEA-NSs solution after different reduction time with a proportion of HAuCl₄ and nanosheets (w/w) 1:6 at 40 $^{\circ}$ C (a) and 60 $^{\circ}$ C (b), as well as the corresponding absorption of these solutions depend on reduction time (c).



Figure S2. The AFM images of AuNP@hPEA-NSs and the height profile along the line of the AFM image, the proportion of HAuCl₄ and nanosheets (w/w) in feed is 1:12.

The decoration of MNPs on hPEA-NSs was further supported by the change of fluorescence of hPEA-NSs aqueous solution. hPEA-NSs are fluorescent as a result of the existence of undimerized AN moieties. Interestingly, we also found that the fluorescence emission of hPEA-NSs could be quenched by AuNPs decorated on the nanosheets. AuNP@hPEA-NSs aqueous solutions with different amounts of HAuCl₄ addition were prepared, and the amount of the AuNPs formed can be estimated by UV-vis spectra (Figure S3a). The fluorescence emission intensity of the AuNP@hPEA-NSs decreases with the increase of the concentration of AuNPs (Figure S3b). This phenomenon can be ascribed to the interaction between the excited fluorophore and the surface-bound metal nanoparticles. As a result, the fluorescence of hPEA-NSs will be quenched because of photoinduced electron transfer from the AN units to the proximate AuNPs.^{2, 3} Similarly, the fluorescence emission of AN units can also be gradually quenched by AgNPs decorated on hPEA-NSs for the same reason (Figure S4). The quenching effect of the fluorescence of hPEA-NSs by MNPs can also confirm that these MNPs are fixed on the surface of the hybrid nanosheets, which is in good agreement with the observation of TEM.



Figure S3. (a) The UV-vis absorption spectra of AuNP@hPEA-NSs aqueous solutions with different proportions of nanosheets and HAuCl₄ (w/w). (b) The fluorescence emission spectra of AuNP@hPEA-NSs aqueous solutions with different proportions of nanosheets and HAuCl₄ (w/w) and their photographs under natural light illumination as well as under 365 nm UV-light illumination in the dark.



Figure S4. (a) The UV-vis absorption spectra of AgNP@hPEA-NSs aqueous solutions (the absorption of hPEA-NSs is subtracted from the spectra) with different proportions of nanosheets and AgNO₃ (w/w). (b) The fluorescence emission spectra of AgNP@hPEA-NSs aqueous solutions with different proportions of nanosheets and AgNO₃ (w/w) and their photographs under natural light illumination as well as under 365 nm UV-light illumination in the dark.



Figure S5. The photograph of AuNP@hPEA-NSs aqueous solutions after stayed at room temperature for a month. The concentration of AuNP@hPEA-NSs in water is 500 mg/L.



Figure S6. (a) Z-Average diameters of AuNP@hPEA-NSs aqueous solutions at different temperatures obtained by DLS with different NaCl concentrations (pH = 5.0). (b) Z-Average diameters of AuNP@hPEA-NSs aqueous solutions at different temperatures obtained by DLS with different pH values.



Figure S7. The dependence of SPR peak of AuNP@hPEA-NSs aqueous solution (pH=5.0) on temperature. Inset: The UV-vis absorption spectra of AuNP@hPEA-NSs aqueous solution (pH=5.0) at different temperatures.



Figure S8. The structure of hPEA which can form nanospheres with an average diameter of ~80 nm and the photograph of AuNP decorated on hPEA nanospheres without POSS moieties (pH=7.0) transferring from water phase to toluene phase upon heating from 25 $^{\circ}$ C to 75 $^{\circ}$ C. The concentration of hPEA nanospheres in water is 500 mg/L.

AgNP@hPEA-NSs were used as a catalyst via the reduction of p-nitrophenol (Nip) in the presence of NaBH₄ as the reductant, which is typically a model reaction for the evaluation of the catalytic ability.⁴ The reaction process was monitored by UV-vis spectra shown in Figure S9. The strong absorption band of p-nitrophenolate ions at 400 nm decreases as reaction time proceeds after adding AgNP@hPEA-NSs; simultaneously, a new peak at 300 nm appears, which is due to the generation of 4-aminophenol. The conversion of the reduction process can be obtained by the ratio of the respective absorption A/A₀, and the time-conversion plot is also shown in Figure S9. The reaction can be described by a first-order rate law, and the apparent rate constant k_{app} is calculated from the slope of the straight line, which is 0.032 min⁻¹. As the dispersion of the MNP@hPEA-NSs in aqueous solution could be controlled by temperature, these nanosheets could be easily recycled after the catalysis process, resulting in the potential of MNP@hPEA-NSs as catalyst.



Figure S9. The UV-vis absorption spectra of the p-nitrophenol (Nip) solution as a function of time during the reduction catalyzed by AgNP@hPEA-NSs at 25 °C, the absorption of AgNPs is subtracted from the spectra. Inset: time-conversion plot of the reduction of Nip catalyzed by AgNP@hPEA-NSs at 25 °C.

Reference

- 1. B. Yu, X. Jiang and J. Yin, *Macromolecules*, 2012, **45**, 7135-7142.
- 2. C. Park, M. S. Im, S. Lee, J. Lim and C. Kim, *Angew Chem Int Ed*, 2008, **47**, 9922-9926.
- 3. Z. Wang, A. G. Skirtach, Y. Xie, M. Liu, H. Möhwald and C. Gao, *Chem Mater*, 2011, **23**, 4741-4747.
- 4. P. Herves, M. Perez-Lorenzo, L. M. Liz-Marzan, J. Dzubiella, Y. Lu and M. Ballauff, *Chem Soc Rev*, 2012, **41**, 5577-5587.