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Supporting Information

Novel Hollow and Yolk-Shell Structured Periodic Mesoporous Polymer Nanoparticles

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Sample preparation

Synthesis of functionalized SiO_2-CHO nanoparticles. In a typical synthesis, 1.7 mL of tetraethyl orthosilicate mixed with 30 mL of ethanol was added to a solution containing 20 mL of ethanol, 6 mL of deionized water and 4 mL of ammonia aqueous solution under stirring. After stirring 5 h at 26 °C, 0.15 mL of 3-(methylacryloxyl)propyltrimethoxysilane dissolved in 100 ml of ethanol was dropped into the reaction solution. The mixture was continuously stirred for 48 h at 26 °C. After centrifugation and washed with ethanol for several times, then dried, the amine-terminated SiO_2-NH_2 nanoparticles were obtained. Subsequently, the SiO_2-NH_2 nanoparticles were redispersed in 150 mL of ethanol, followed by addition of 2 mL of 25% glutaraldehyde aqueous solution. After stirring for 2 h at 80 °C, the aldehyde-terminated SiO_2-CHO nanoparticles were collected by centrifugation, and then washed with water and ethanol for several times.

Synthesis of resol-F127 composite solution. Typically, 0.61 g of phenol was mixed with 15 mL of 0.1 mol L^{-1} NaOH aqueous solution under stirring. Then, 2.1 mL of 37 wt.%

formaldehyde solution was added. After that, the clear mixture was reacted under stirring for 0.5 h at 70 ^{o}C and then was cooled to room temperature to obtain phenolic resols. Subsequently, 0.96 g of of triblock copolymer F127 dissolved in 65 mL of H_2O was mixed with the above phenolic resols. The resultant mixture was stirred continuously at 65 °C with a stirring speed of 340 ± 5 rpm for 13 h, resulting in resol-F127 composite solution.

*Synthesis of hollow periodic mesoporous polymer nanoparticles***.** Typically, 0.30 g of SiO_2-CHO nanoparticles dispersed in 150 mL of deionized water was added to 40 mL of the resol-F127 composite solution, followed by stirring continuously at 65 °C with a stirring speed of 400± 5 rpm for 6 h. The obtained mixture was transferred into autoclave and hydrothermally treated for 24 h at 130 °C. The as-made SiO_2@polymer nanoparticles were obtained by centrifugation, then washed with water and ethanol for several times, and dried at 50 °C. The as-made organic/inorganic hybrid nanoparticle sample was calcined under N_2 flow at 350 ^{o}C for 3 h to decompose the F127 template and obtain the core-shell structured SiO_2@PMPNPs. The heating rate was 1 ^{o}C min^{-1}. The resulting SiO_2@polymer nanocomposite was treated using HF aqueous solution to remove SiO_2, washed, filtrated and then dried, leading to formation of HPMPNPs. For comparison, a control polymer sample was synthesized. Its preparation procedure was exactly the same as that of the HPMPNPs except that the unfunctionalized SiO_2 nanoparticles were employed.

Synthesis of Au@SiO_2 core-shell nanoparticles. Briefly, 975 mL of deionized water was vigorously stirred under reflux and 0.086 g of $HAuCl_4$ was added. The resultant solution was stirred until its boiling point was reached again. Then, 0.50 g of sodium citrate dissolved in 20 mL of deionized water was added, followed by refluxed for 30 min and then cooled down to room temperature. Subsequently, 0.017 g of polyvinylpyrrolidone dissolved in 5 mL of deionized water was added to the above mixture and stirred for 24 h at room temperature. The resulting dispersion was centrifuged and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 24 mL by dilution with water. For SiO_2 coating, 12 mL of the as-obtained Au nanoparticles in water was mixed with 38 mL of ethanol, followed by an ultrasonic mixing for 30 min. Then 1 mL of ammonia aqueous solution was added and mechanically stirred. After 10 min, a solution of 2.4 mL of TEOS in 7 mL of ethanol was injected into the solution. The reaction was performed for 12 h. The product was collected by centrifugation, washed with water and ethanol for several times, and then dried, leading to formation of the Au@SiO_2 core-shell nanoparticles.

Synthesis of functionalized Au@SiO_2-CHO nanoparticles. Typically, 0.3 g of the as-obtained Au@SiO_2 nanoparticles was desipersed in a solution containing 100 mL of ethanol, 10 mL of deionized water and 1 mL of ammonia aqueous solution. Then 1 mL of 3-(methylacryloxyl) propyltrimethoxy silane dissolved in 50 ml of ethanol was dropped into the reaction solution. The mixture was continuously stirred for 48 h at 27 °C. The product was collected by centrifugation, washed with ethanol for several times, and then dried, leading to formation of the amine-terminated Au@SiO_2-NH_2 nanoparticles. Subsequently, the Au@SiO_2-NH_2 nanoparticles were redispersed in 150 mL of ethanol, followed by addition of 2 mL of 25% glutaraldehyde aqueous solution. After stirring 2 h at 80 °C, the as-obtained aldehyde-terminated Au@SiO_2-CHO nanoparticles were collected by centrifugation, washed with water and ethanol for several times, and then dried.

Synthesis of yolk-shell structured Au@periodic mesoporous polymer nanoparticles. Typically, 0.21 g of the as-prepared Au@SiO_2-CHO dispersed in 150 mL of deionized water was added to 50 mL of resol-F127 composite solution. The mixture was stirred at 65 °C with a stirring speed of 400± 5 rpm for 6 h. The obtained mixture was transferred into autoclave and hydrothermally treated for 24 h at 130 °C. After cooling down, the solid hybrid nanoparticles were obtained by centrifugation, washed with water and ethanol for several times, and then dried at 50 °C in air. The as-made hybrid nanoparticle sample was calcined under N_2 flow at 350 ^{o}C for 3 h to decompose the F127 template, thus obtaining the Au@SiO_2@PMPNP core-shell-shell nanoparticles. The heating rate was 1 ^{o}C min^{-1}. The resulting nanocomposite was treated using HF aqueous solution to remove SiO_2, washed, filtrated and then dried, leading to formation of yolk-shell structured Au@PMPNPs.

Synthesis of hollow disordered microporous polymer nanoparticles. Hollow disordered microporous polymeric nanoparticles with diamter of 265 nm were synthesized following the procedure reported previously.[1]

Characterization.

Material characterization. The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM) and a FEI Tecnai G2 Spirit transmission electron microscope (TEM). About 100 nanoparticles in a SEM image were picked at random, and then a statistical analysis of the particle size distribution was carried out. The maximum in the resulting particle size distribution curve was referred to as the diameter of nanoparticles. XRD patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu K radiation. The FTIR measurements of the samples were performed with IR spectroscopy (Bruker TENSOR 27), using KBr disk method. Nitrogen adsorption measurements were carried out using a Micromeritics ASAP 2020 analyzer at 77K. The BET surface area was analyzed by Brunauer-Emmett-Teller (BET) theory. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. The total pore volume (V_t) was calculated according to the amount adsorbed at a relative pressure P/P_0 of about 0.99. Dynamic light scattering (DLS) measurements were carried out at 25 °C on a Brookheaven Zeta PALS Instrument with a 532 nm laser at a scattering angle of 90°, providing the PDI and hydrodynamic diameter (*i.e.*, the maximum in the DLS particle size distribution curve).

Adsorption properties toward methanol vapor. The adsorption properties toward methanol vapor were studied with a Hiden IG-3 intelligent gravimetric analyzer. The adsorption rate test was performed under 5 mb methanol vapor.

Adsorption properties toward vitamin B12. 50 mg of carbon powder was added into a conical flask, and then 10 mL of VB12 solution (20 mg/L) was added quickly. After that, this suspension was stirred at 35 °C.

Catalytic reduction of nitrobenzene and 4-nitrophenol. The catalytic reduction of nitrobenzene and 4-nitrophenol were studied with a UV-Vis-NIR spectrophotometer. About 10 mg of Au@PMPNP was homogeneously dispersed in 8 mL of ethanol by ultrasonication. Then, 0.5 ml of the obtained Au@PMPNP/ethanol suspension was added to a mixture containing sodium borohydride solution (1 mL, 0.1 mM) and 4-nitrophenol or nitrobenzene solution (2 mL, 0.11 mM). After that, the reaction progress was monitored by measuring UV-vis absorption spectra of the mixture.

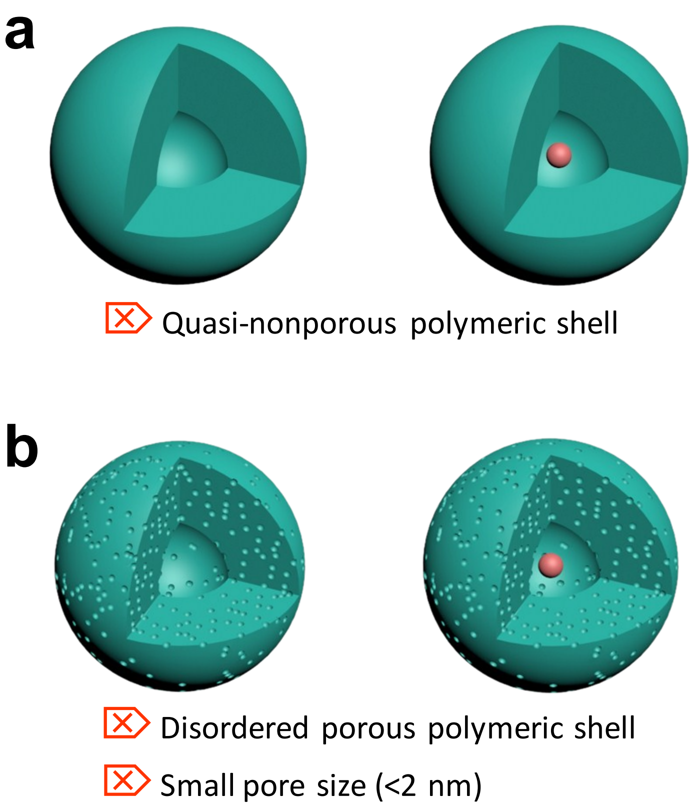

Fig. S1 Schematic illustration of the conventional hollow (left) and yolk-shell structured (right) polymer nanoparticles. For these polymer nanoparticles, their shell always possesses (a) quasi-nonporous structure or (b) highly disordered pore structure with small-sized pores (< 2 nm).

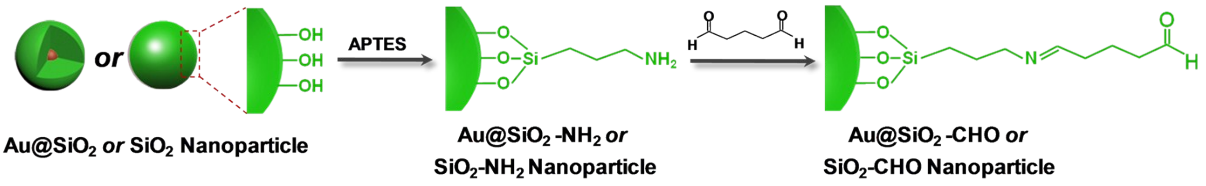

Fig. S2 Synthetic route to SiO_2 and Au@SiO_2 nanoparticles with functional aldehyde groups.

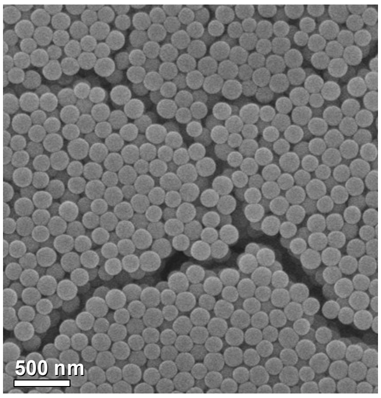

Fig. S3 SEM image of conventional SiO_2 nanoparticles.

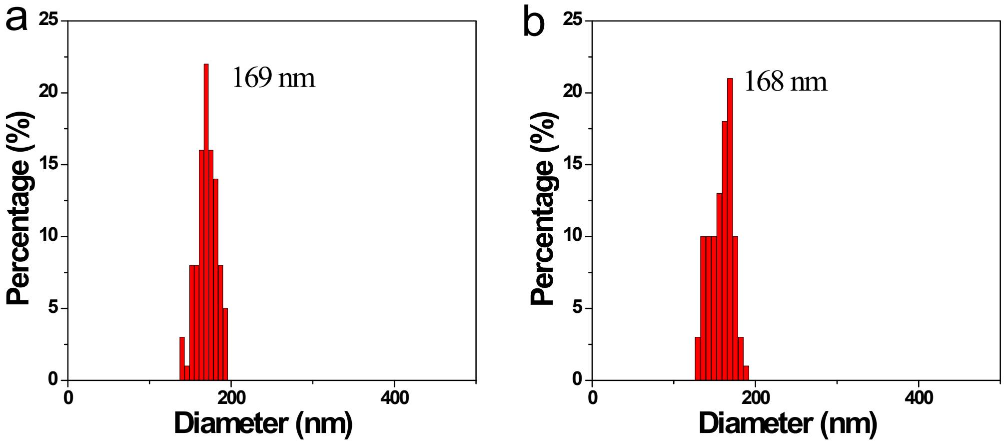

Fig. S4 Particle size distribution histogram from SEM image analysis for (a) conventional SiO_2 nanoparticles and (b) SiO_2 nanoparticles with functional aldehyde groups. The resulting SiO_2 nanoparticles with functional aldehyde groups have almost the same particle diameter and monodispersity as their parent SiO_2 nanoparticles, illuminating that the functionalization reaction essentially does not change the morphology.

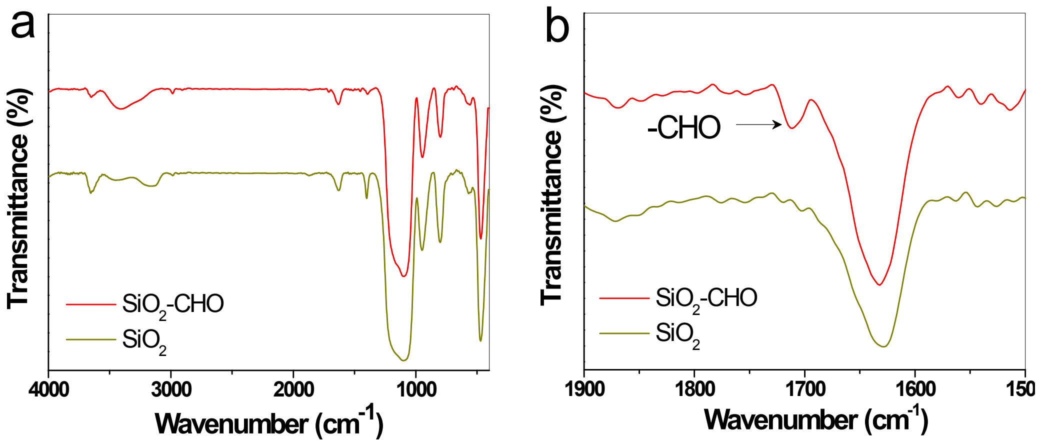

Fig. S5 Fourier-transform infrared spectrums of conventional SiO_2 nanoparticles and SiO_2 nanoparticles with functional aldehyde groups. After functionalization reaction, the characteristic of absorption peak of the -CHO group is observed at 1713 cm^{-1} in the FTIR spectrum.[2] These results clearly point to the successful introduction of aldehyde groups onto the surface of SiO_2 nanoparticles.

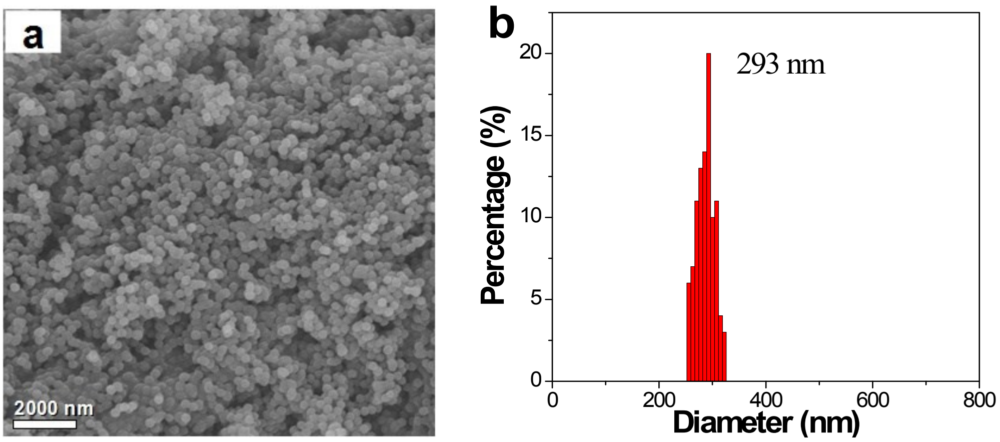

Fig. S6 (a) SEM image and (b) particle size distribution histogram from SEM image analysis for as-made SiO_2@polymer nanoparticles. The as-made SiO_2@polymer nanoparticles display a uniform spherical morphology with a diamter of about 293 nm.

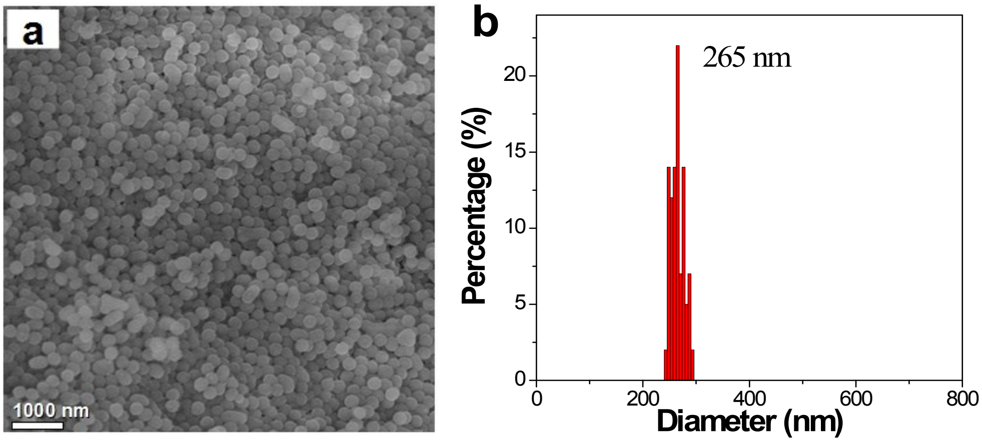

Fig. S7 (a) SEM image and (b) particle size distribution histogram from SEM image analysis for SiO_2@PMPNP. The diamter of SiO_2@PMPNP reduces to 265 nm after a high-temperature (*i.e.*, 350 °C) heating treatment, indicative of a little framework shrinkage.

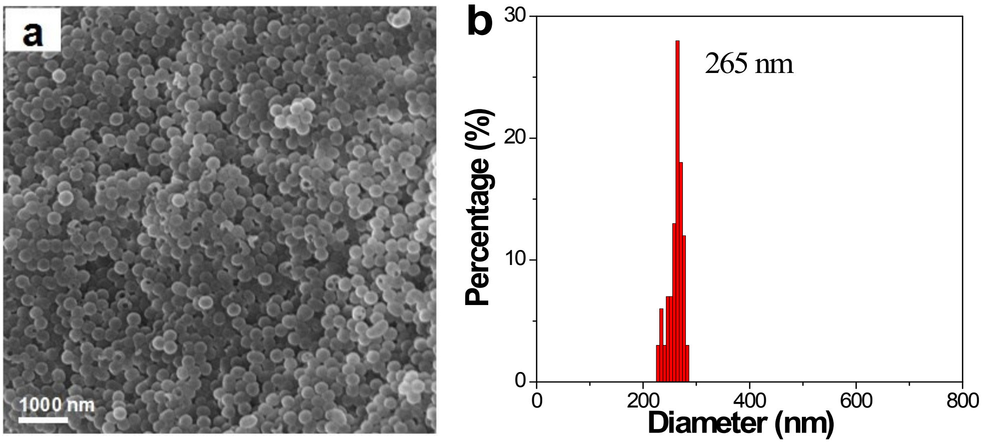

Fig. S8 (a) SEM image and (b) particle size distribution histogram from SEM image analysis for HPMPNP. HPMPNP has uniform spherical morphology with a monodisperse size distribution of 265 nm.

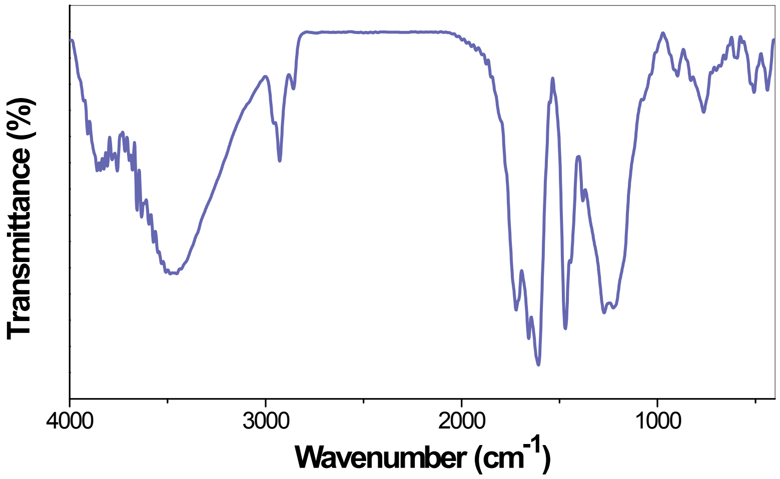

Fig. S9 FTIR spectrum of HPMPNP. FTIR spectroscopy is used to determine the chemical nature of the periodic polymeric shell. It can be noticed that the peaks in the range 1100~1300 cm^{-1} due to various C-O-C linkages show strong intensity. The band at 1610 cm^{-1} is also observed, which is caused by the quadrant aromatic ring-stretching of 1,2,4- and 1,2,6-trisubstitued and phenyl alkyl ether-type substituted aromatic ring structures.[3] The bands at 1470 and 2930 cm^{-1} can be assigned to the vibration of the C-H stretching of methylene group. These analyses confirm that the shell framework of HPMPNP is composed of network phenolic resin from condensation polymerization of phenol and formaldehyde. [4]

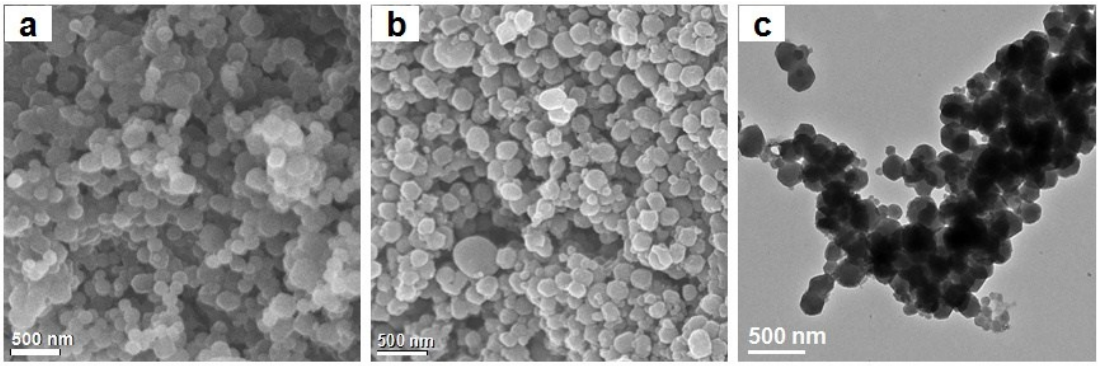

Fig. S10 SEM images of (a) the polymer/SiO_2 composite and (b) the polymer sample prepared by using the conventional SiO_2 nanoparticle as the template. (c) TEM image of the polymer sample showing its totally solid nanoparticle characteristic.

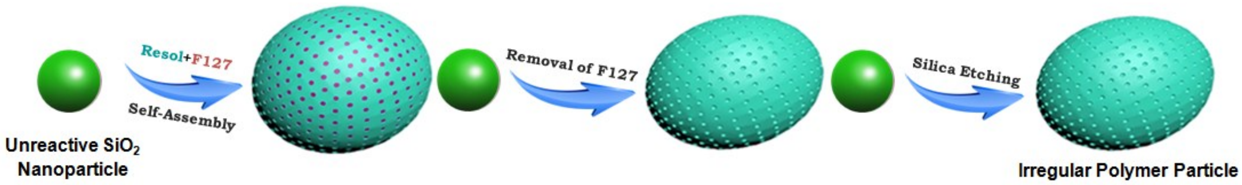

Fig. S11 Schematic diagram of the failed cooperative assembly of resol and F127 on a conventional unreactive SiO_2 nanoparticle because of their weak interaction.

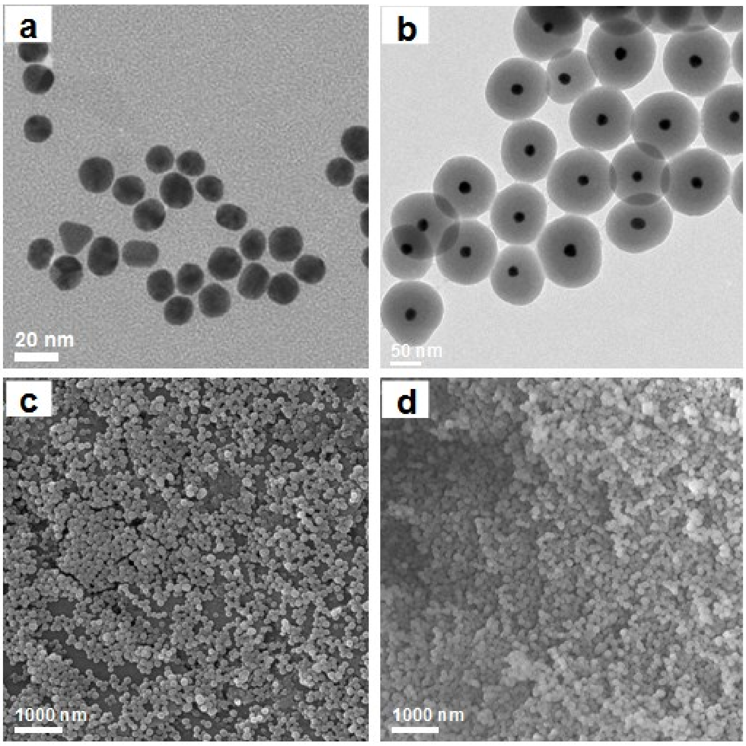

Fig. S12 TEM images of (a) Au nanoparticle with diameter of *ca.* 20 nm and (b) the bare Au@SiO_2 core-shell nanoparticles. SEM images of (c) the bare Au@SiO_2 core-shell nanoparticles and (d) the functionalized Au@SiO_2-CHO core-shell nanoparticles.

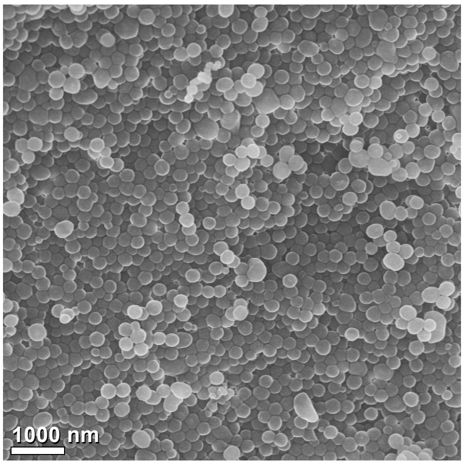

Fig. S13 SEM image of Au@SiO_2@PMPNPs core-shell-shell nanoparticles. The as-prepared Au@SiO_2@PMPNP shows uniform spherical morphology with a diameter of about 250 nm.

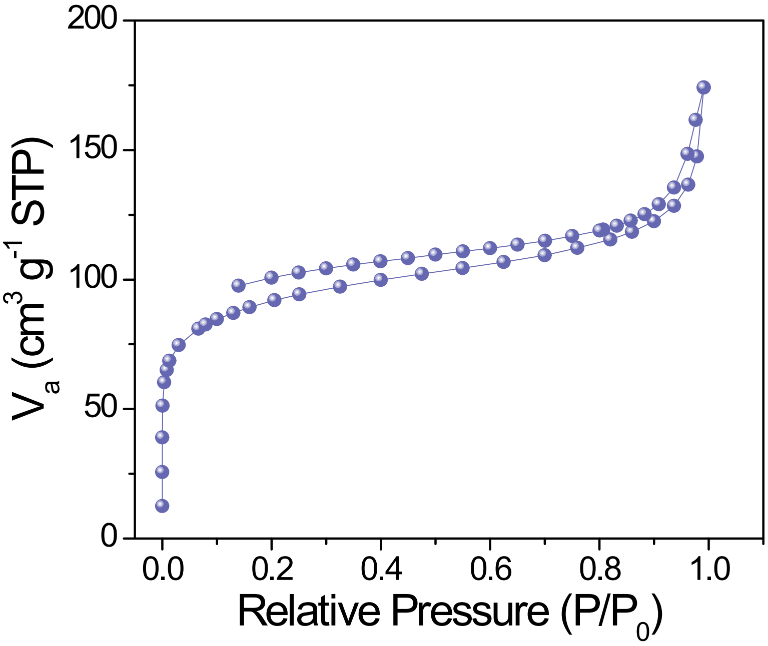

Fig. S14 Nitrogen adsorption-desorption isotherm of HDMPNP. An obvious adsorption uptake at low relative pressure is observed, implying a robust micropore structure. BET calculation gives the BET surface area for HDMPNP equal to 335 m^2 g^{-1}, and the total pore volume is calculated to be 0.27 cm^3 g^{-1} according to the amount adsorbed at a relative pressure P/P_0 of *ca.* 0.99.

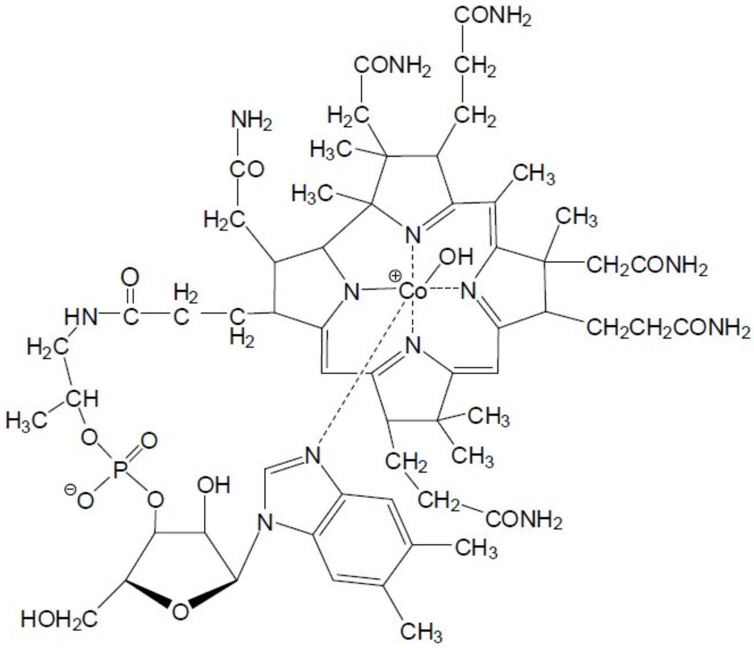

Fig. S15 Structural formula of VB12. The VB12 has molecular dimensions of 1.84 nm ×1.41 nm × 1.14 nm.[5]

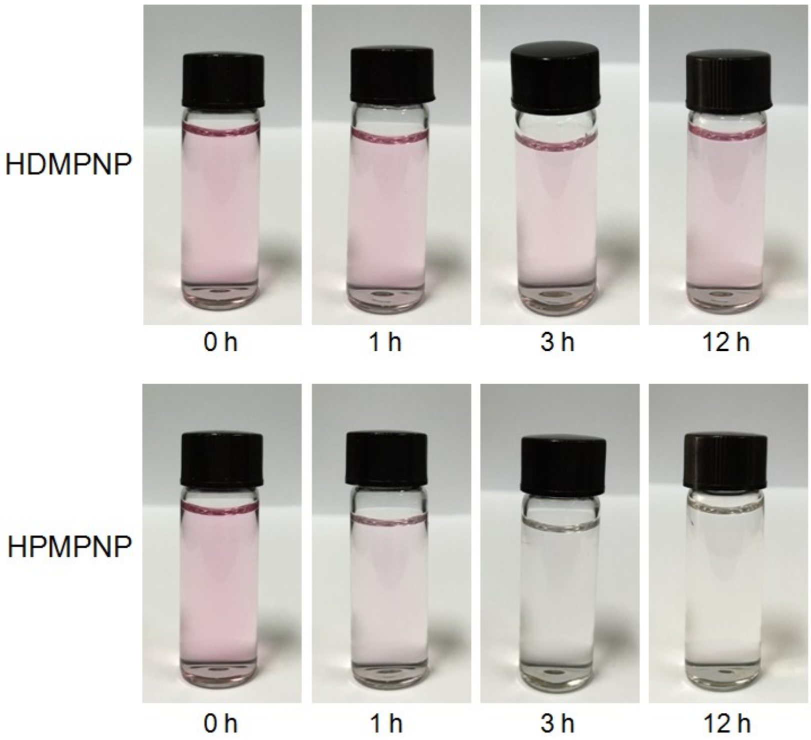

Fig. S16 Digital photos of the filtered solutions of VB12 after exposure to HDMPNP and HPMPNP for various time.

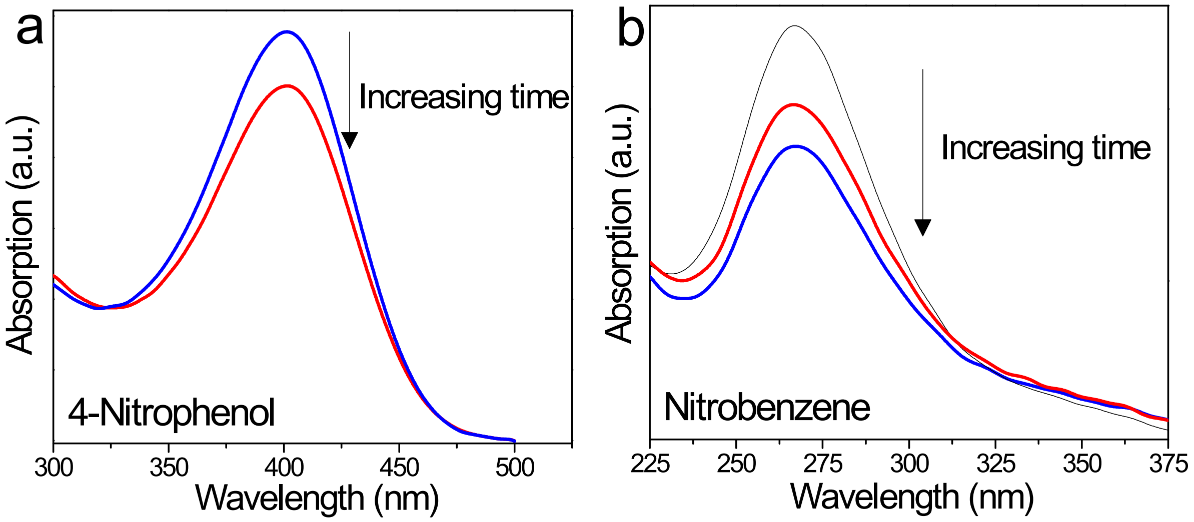

Fig. S17 UV-vis spectra showing gradual reduction of (a) 4-nitrophenol and (b) nitrobenzene with Au@PMPNP. The absorption peak of 4-nitrophenol at 400 nm decreases with reaction time, which indicates the 4-nitrophenol is reduced. The complete conversion of 4-nitrophenol could also be visually appreciated by the color change of the solution from yellow to clear. In contrast, no change in the absorbance of a solution of 4-nitrophenol is detected in the absence of catalyst. For the reduction of nitrobenzene, the characteristic absorption peak of nitrobenzene at 270 nm weakens with reaction time, resulting from the successful reduction of nitrobenzene.

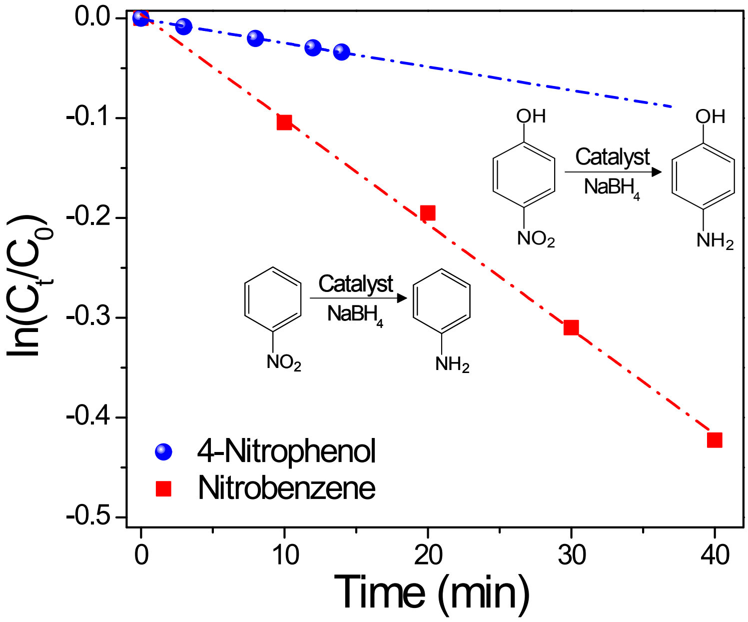

Fig. S18 Plots of $\ln(C_t/C_0)$ versus timefor the catalytic reduction of nitrobenzene and 4-nitrophenol with Au@PMPNP as the catalyst. A linear relationship of $\ln(C_t/C_0)$ versus time is observed for the Au@PMPNP, suggesting that the reduction reaction follows a pseudo-first-order kinetics.

References

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