

## Supporting Information

# Core/Shell to Yolk/Shell Nanostructures by a Novel Sacrificial Template-Free Strategy

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### **EXPERIMENTAL PART**

*o*-Methoxyaniline and *o*-toluidine monomers were distilled under reduced pressure. All other reagents were received without further purification. The water used in this study was deionized by milli-Q Plus system (Millipore, France), having 18.2 MΩ electrical resistivity.

*Synthetic Procedure:* (1) Synthesis of Au colloids: The synthesis of Au colloids was according to the literature.<sup>1</sup> Deionized water (102 ml) was vigorously stirred under reflux and a HAuCl<sub>4</sub> solution (12 ml, 2.54 mM) was added. The resultant solution was stirred until boiling point was reached again. Then, a sodium citrate solution (6 ml, 10 mg ml<sup>-1</sup>) was added and the system was refluxed for 30 min, and finally, the resultant colloid was cooled to room temperature. The suspension was washed with deionized water three times by using centrifuge and then redispersed in 67 ml deionized water for

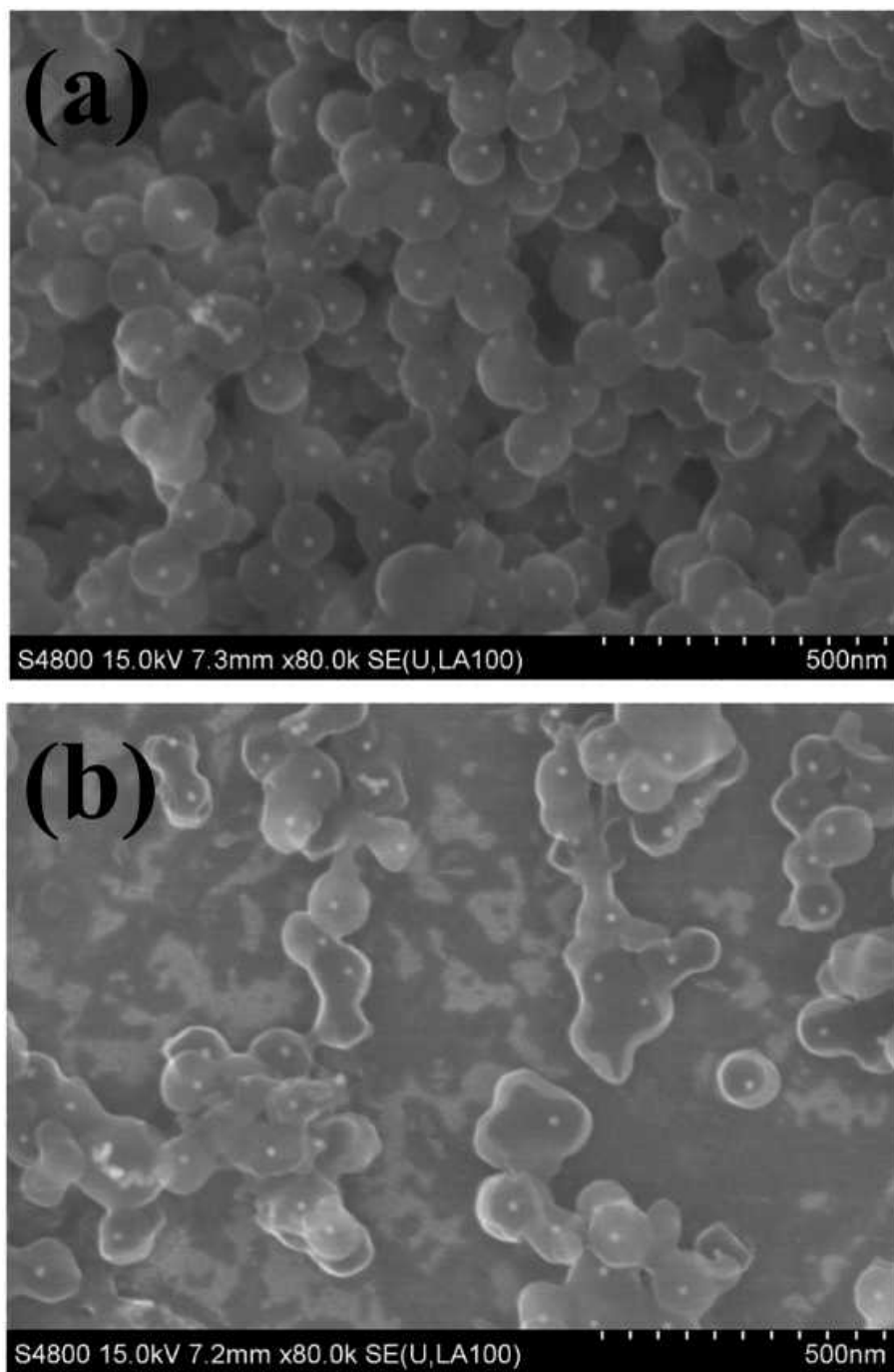
further use. The average size of Au nanoparticles is 15 nm. (2) Synthesis of Ag colloids: The synthesis of Ag colloids was according to the literature.<sup>2</sup> An aqueous solution of AgNO<sub>3</sub> (0.75 mM, 100 mL) was heated to boil and then sodium citrate solution (1% w/v) was added with vigorous stirring. Continuing heating for 30 min yielded a turbid and greenish yellow solution of Ag colloids, which was subsequently diluted by a factor of 10. To remove the residual agents, the Ag colloids solution was centrifuged at 8000 rpm for 10 min and then redispersed in 100 ml deionized water for further use. (3) Synthesis of Au/POMA core/shell nanostructures: In a typical synthesis, 10.0 mg *o*-methoxyaniline and 0.010 g F127 were dispersed in freshly synthesized 5.0 ml gold colloids with magnetic stirring at room temperature for 1.0 h. After that, the mixture was maintained at 20 °C for 0.5 h before oxidative polymerization. Then the aqueous solution of APS (20 wt%, maintaining molar ratio of monomer to APS at 1:1) was added to the above mixture in one portion. The reaction was allowed to proceed with agitation for 2.0 h at 20 °C. Finally, the products were washed with deionized water till the filtrate became colorless and then redispersed in excess deionized water. (4) Synthesis of Au/POMA yolk/shell nanostructures: The synthesized Au/POMA core/shell nanostructures as described above were centrifuged, suspended in excess ethanol and then were swelled by the solvent for a certain time. After that, the swollen Au/POMA core/shell nanostructures were placed under room temperature and pressure to let the solvent evaporate. After complete evaporation, Au/POMA yolk/shell nanostructures can be formed.

*Characterization:* Morphologies of products were examined by a field-emission scanning electron microscope (FESEM, S-4800, Hitachi Co., Japan) and a transmission electron microscope (TEM, Tecnai-12 Philip Apparatus Co., USA), respectively. Samples for TEM measurements were deposited on copper grids. XRD patterns were recorded on a German Bruker AXS D8 ADVANCE X-ray diffractometer. The products were recorded in the 2 $\theta$  range from 10° to 85.0° in steps of 0.04° with a count time of 1 s each time. The FTIR spectra (Nicolet-740 America) were recorded in the range of 400 ~ 4000 cm<sup>-1</sup>. The samples were prepared in pellet form with spectroscopic-grade KBr. The ultraviolet-visible (Uv-vis) spectra (UV-2501, Shimadzu Corporation, Japan) of products dissolved in water was measured in the range between 250 and 800 nm.

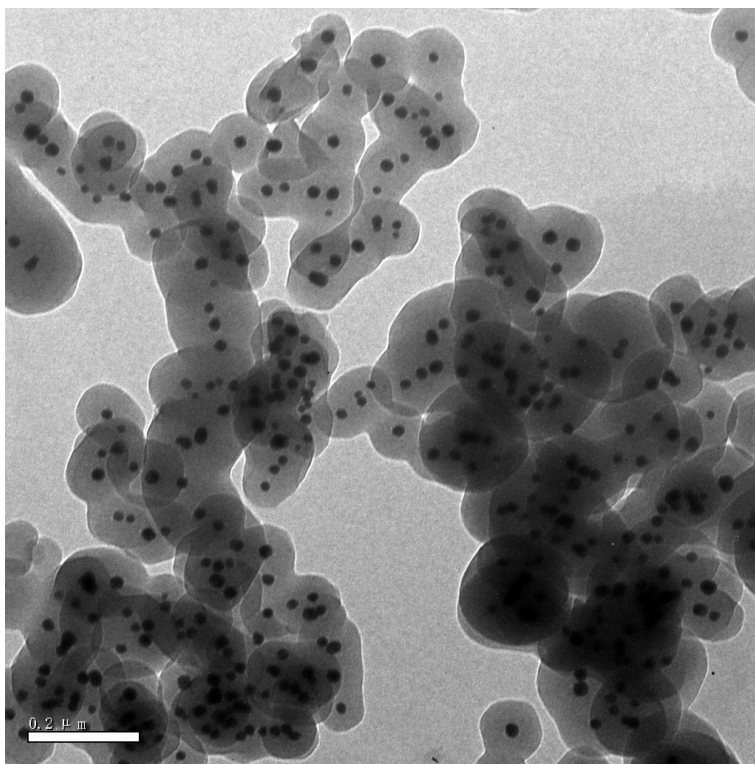
*Catalytic Test:* Typically, aqueous solution of NaBH<sub>4</sub> (1.0 mL,  $1.5 \times 10^{-2}$  M) was mixed with aqueous 4-NP solution (1.7 mL,  $2.0 \times 10^{-4}$  M) in the quartz cell (1 cm path length), leading a color change from light yellow to yellow-green. Then, gold catalysts (0.3 mL,  $2.0 \times 10^{-4}$  M) were added to the mixture and quickly placed in the cell holder of the spectrophotometer. The progress of the conversion of 4-NP to 4-AP was then monitored via the Uv-vis spectroscopy by recording the time-dependent absorption spectra of the reaction mixture with a certain time interval in a scanning range of 250-600 nm at ambient temperature. N<sub>2</sub> adsorption-desorption measurements were conducted using Thermo Sorptomatic 1990 by N<sub>2</sub> physisorption at 77 K. The as-calcined samples were out gassed for 4 h at 250 °C under vacuum ( $p < 10^{-2}$  Pa) in the degas port of the sorption analyzer. The BET specific surface areas of samples were evaluated using adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions were calculated from the adsorption branch of the isotherm using the thermodynamic-based Barrett-Joyner-Halenda (BJH) method.

## References:

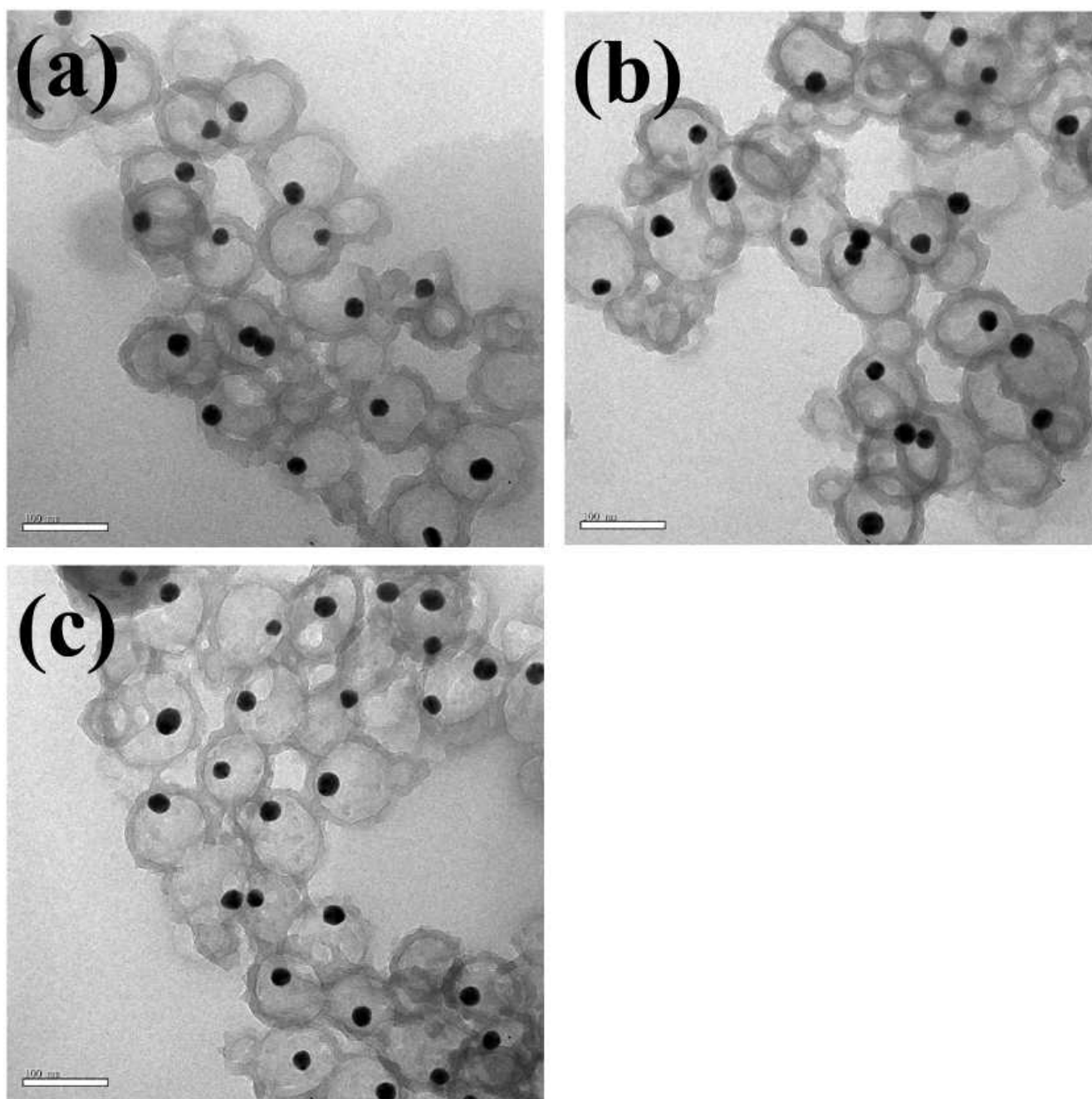
- (1) J. Turkevich, P. L. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55-75.
- (2) P. C. Lee and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391-3395.



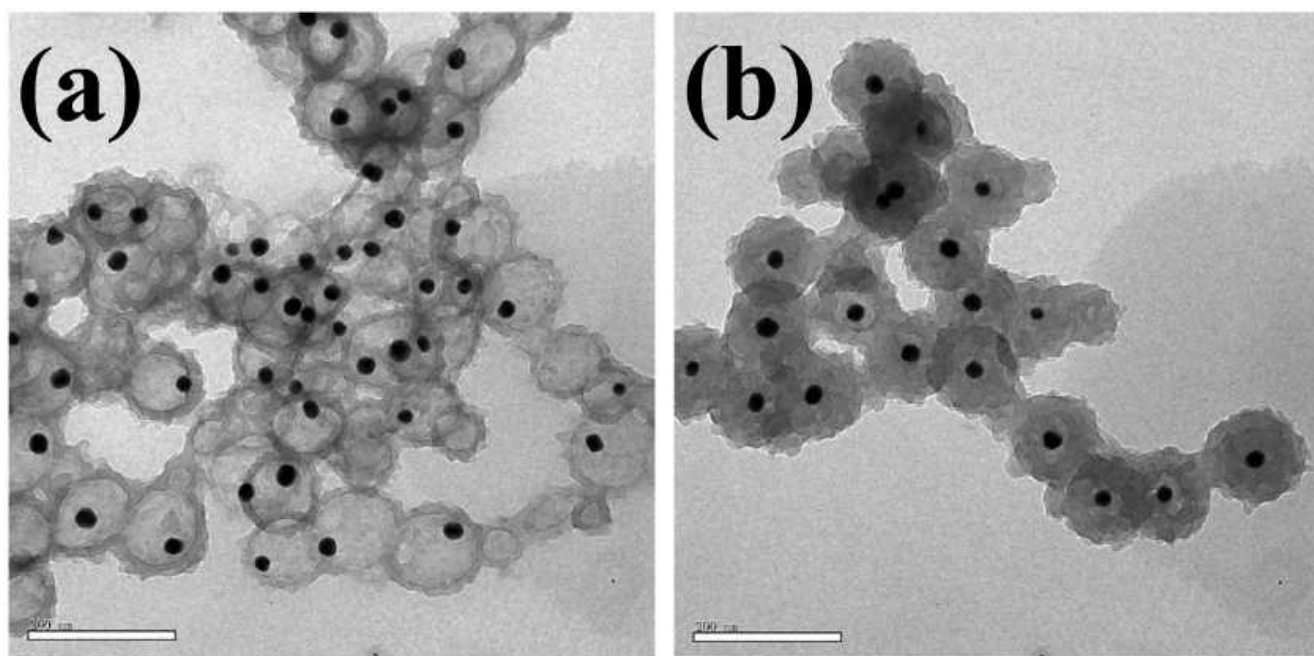
**Fig. S1** Backscattering SEM images of Au/POMA (a) core/shell and (b) yolk/shell nanostructures.



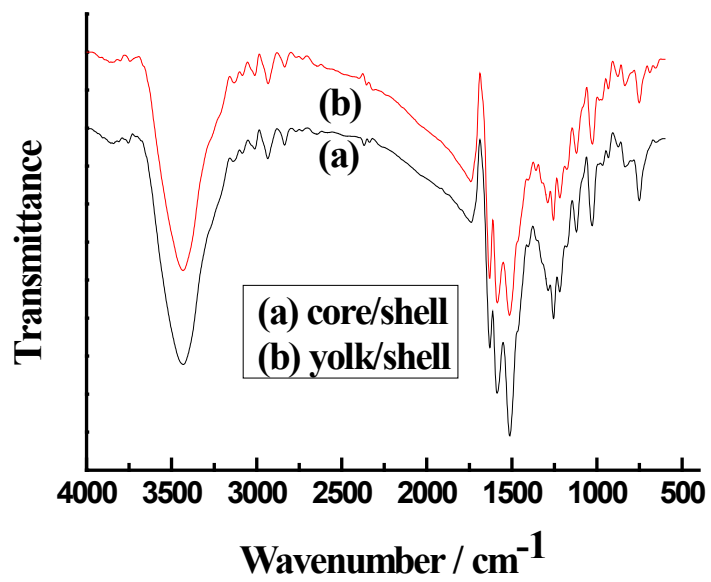
**Fig. S2** TEM image of deformed Au/POMA core/shell nanostructures derived from Au/POMA core/shell nanostructures (Fig. S1) through swelling-evaporation processes using *n*-hexane as the swelling solvent.



**Fig. S3** TEM images of Au/POMA yolk/shell nanostructures derived from Au/POMA core/shell nanostructures (Fig. S1) through swelling-evaporation processes using ethanol solvent at different swelling time: (a) 5 min, (b) 1 h, and (c) 2 h.

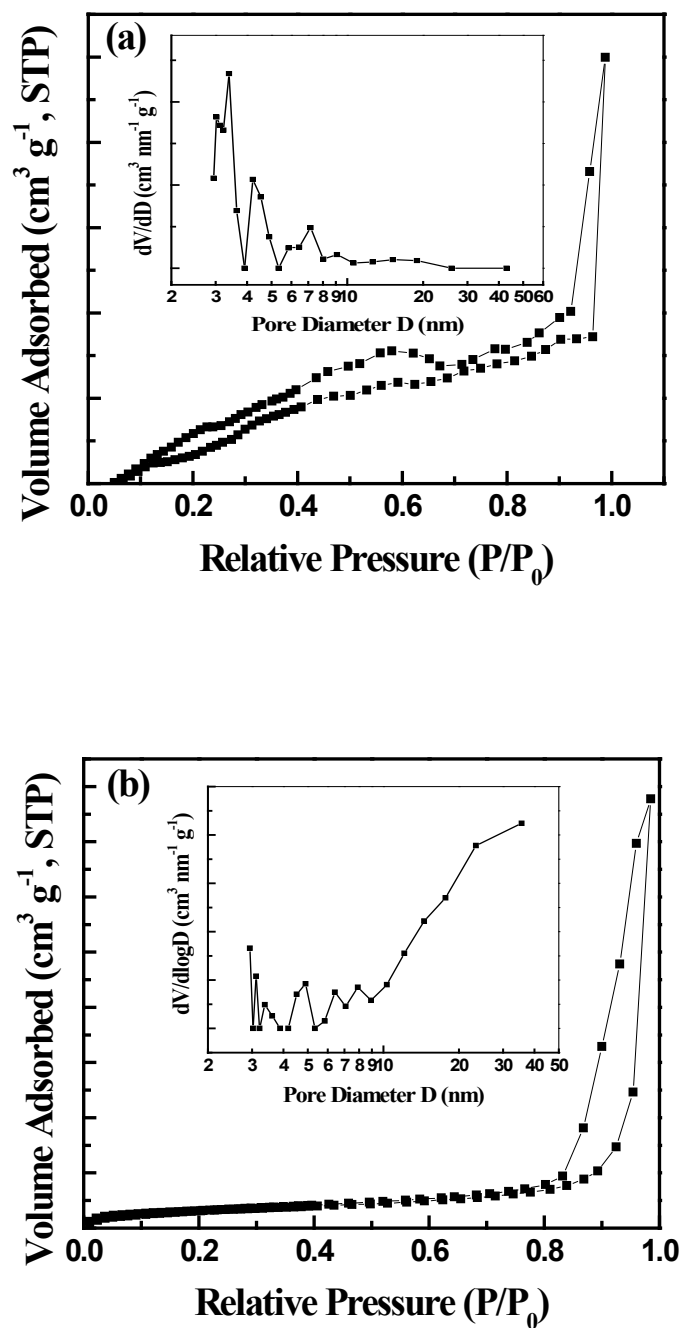


**Fig. S4** TEM images of Au/POMA yolk/shell nanostructures derived from Au/POMA core/shell nanostructures (Fig. S1) through swelling-evaporation processes using ethanol/H<sub>2</sub>O mixed solvent with different volume ratio: (a) 9:1 and (b) 5:5.

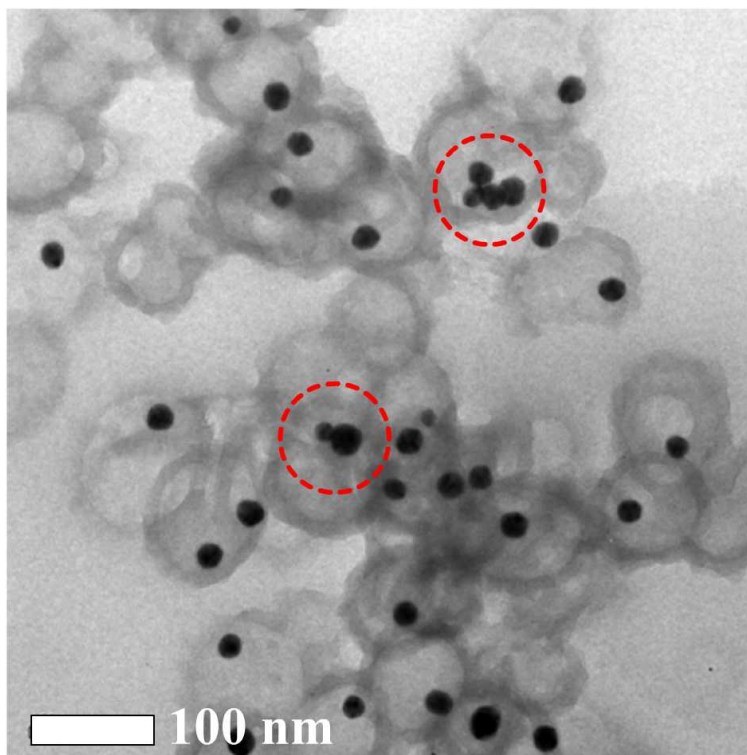


**Fig. S5** FTIR spectra of Au/POMA (a) core/shell and (b) yolk/shell nanostructures.





**Fig. S6** N<sub>2</sub> adsorption-desorption isotherms of Au/POMA (a) core/shell and (b) yolk/shell nanostructures. Insets show corresponding pore size distribution obtained from the BJH model applied to the adsorption branch.



**Fig. S7** TEM image of Au/POMA yolk/shell nanostructures after six runs involved in the catalytic reduction of 4-NP. Red cycles indicate aggregated Au nanoparticles.