

## Supporting Information

# **Reactive Polyaniline-Supported Sub-10-nm Noble Metal Nanoparticles Protected by a Mesoporous Silica Shell: Controllable Synthesis and Application as Efficient Recyclable Catalysts**

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### **EXPERIMENTAL PART**

Aniline monomer (ABCR GmbH & Co. KG) was distilled under reduced pressure. All other reagents were purchased from Aldrich and used without further purification. The water used in this study was deionized by milli-Q Plus system (Millipore, France), having 18.2 M $\Omega$  electrical resistivity.

*Synthetic Procedure:* (1) Synthesis of PS@PANI core@shell nanostructures: Monodisperse polystyrene particles with a diameter of 200 nm were prepared by seed-emulsion polymerization.<sup>1</sup> The freeze-dried polystyrene particles were immersed in large quantity of concentrated sulfuric acid and stirred at 40 °C and for 1 h time, thereby controlling the thickness of the sulfonated-polystyrene-gel shell. After the product was separated by centrifugation, then washed with ethanol, sulfonated PS nanospheres were obtained. In a typical synthesis of PS@PANI core@shell nanostructures, 50 mg sulfonated PS

nanospheres were dispersed in 100 ml deionized water with magnetic stirring at room temperature for 1 h to obtain a uniform colloid solution. Then, 0.15 mL aniline was added to the above mixture. The resulting solution was stirred for 30 min to ensure complete adsorption of aniline on surfaces of PS nanoparticles. After that, 1.875 g ammonium peroxydisulfate aqueous solution (20%) was added in one portion mixing and then the reaction was allowed to proceed under agitation for 24 h at 20 °C. Finally, the PS@PANI core@shell nanoparticles were washed with deionized water and ethanol till the filtrate became colorless and then re-dispersed in 5.0 ml aqueous solution for further use or dried in a vacuum at 60 °C for 24 h for characterization. The yield of PS@PANI core@shell nanostructures was ~80 mg.

(2) Synthesis of PS@PANI@SiO<sub>2</sub> sandwich-like core@shell nanostructures: In a typical synthesis, 1.0 ml of the above-mentioned aqueous solution containing PS@PANI nanoparticles was added into 20.0 ml ethanol, followed by addition of 1 ml ammonia and 0.3 ml tetraethylorthosilicate (TEOS). The resulting solution was allowed to proceed under agitation for 12 h. Finally, the PS@PANI@SiO<sub>2</sub> sandwich-like core@shell nanostructures were washed with ethanol and then re-dispersed in 5.0 ml aqueous solution for further use or dried in a vacuum at 60 °C for 24 h for characterization. The yield of PS@PANI@SiO<sub>2</sub> sandwich-like core@shell nanostructures was ~50 mg.

(3) Synthesis of PS@PANI/m-SiO<sub>2</sub> yolk/shell nanostructures: In a typical synthesis, 1.0 ml of the above-mentioned colloid solution containing PS@PANI@SiO<sub>2</sub> nanoparticles was dilute to 20 ml with deionized water, followed by addition of 0.20 g poly(vinylpyrrolidone) (PVP) K30. The resulting dispersion solution was allowed to proceed under agitation for 12 h. After that, the products were washed with deionized water and then re-dispersed in 20 ml deionized water. Then, 0.350 g NaOH was added into the colloid solution to start the etching for 1.0 h. After washing with deionized water for several times, the finally PS@PANI/m-SiO<sub>2</sub> yolk/shell nanostructures were re-dispersed in 5.0 ml deionized water for further use or dried in a vacuum at 60 °C for 24 h for characterization. The yield of PS@PANI/m-SiO<sub>2</sub> yolk/shell nanostructures was ~8 mg.

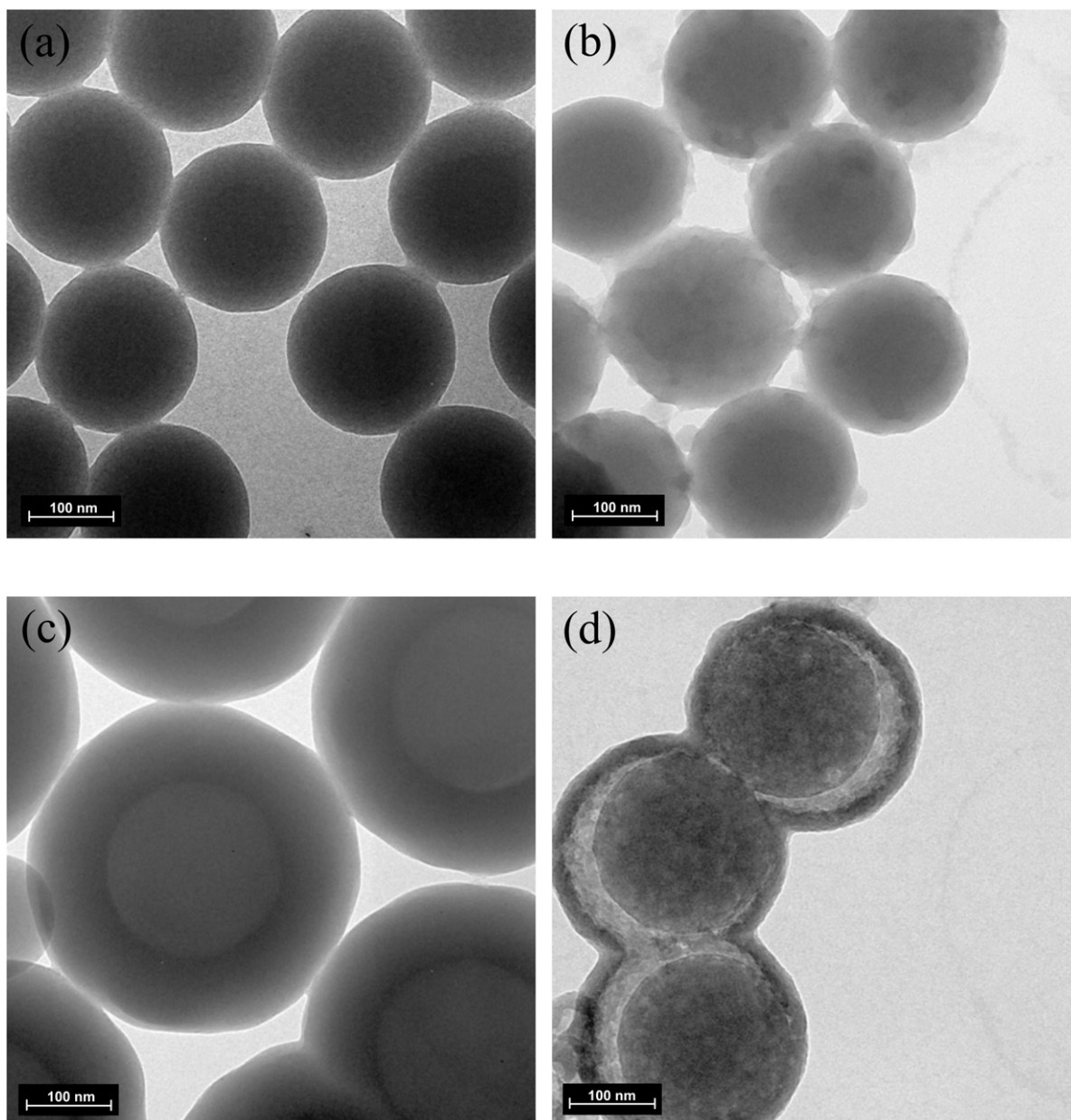
(4) Synthesis of PS@PANI@Au/m-SiO<sub>2</sub> yolk/shell nanostructures: In a typical synthesis, 1.0 ml of the above-mentioned colloid solution containing PS@PANI/m-SiO<sub>2</sub> yolk/shell nanoparticles was dilute to 10 ml with deionized water, followed by addition of a certain

amount of 0.01 M  $\text{HAuCl}_4$  aqueous solution. The resulting dispersion solution was allowed to proceed under agitation for 3 h for complete reaction between gold ions and PANI. Finally,  $\text{PS@PANI@Au/m-SiO}_2$  yolk/shell nanostructures were washed with water and re-dispersed in deionized water for further use as catalysts or dried in a vacuum at 60 °C for 24 h for characterization. After formation of  $\text{PS@PANI@Au/m-SiO}_2$  yolk/shell nanostructures as precipitation at bottom of reaction vessel, the upper solution was analyzed by atomic adsorption spectroscopy to confirm the remaining of unreacted raw materials of gold ions. As detected, the remaining gold ions is neglectable as compared with the initial charge in the given  $\text{HAuCl}_4$  concentration. As a result, the molar of Au nanoparticles in product can be seen as equal as the initial charge.

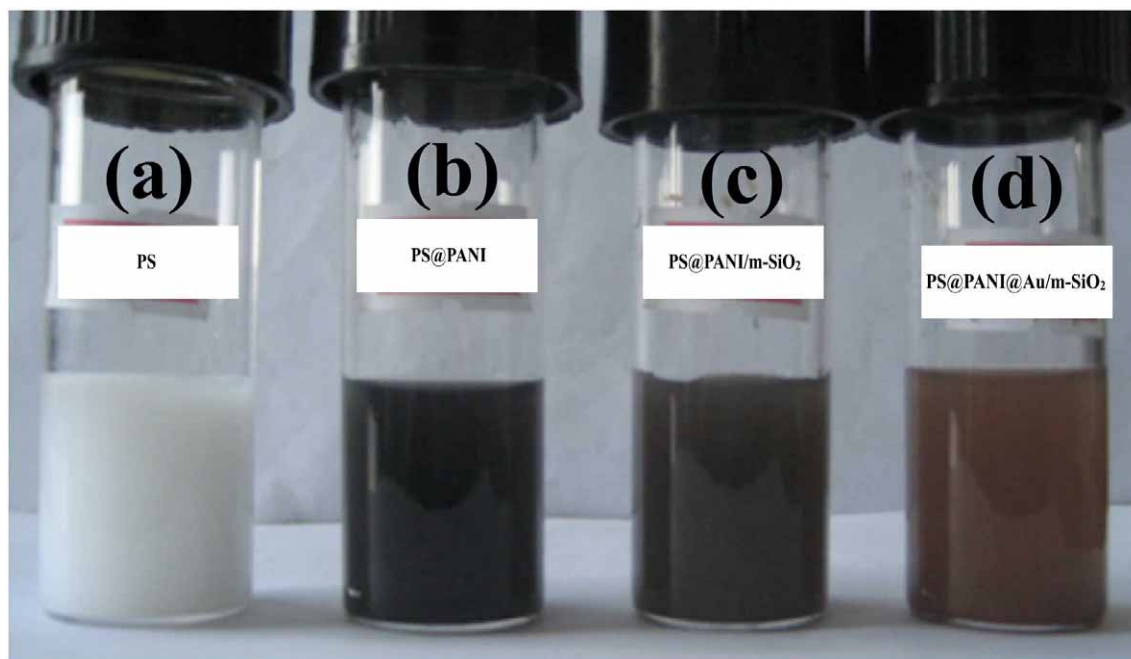
*Characterization:* Morphologies of products were examined by a transmission electron microscope (TEM, Tecnai-12 Philip Apparatus Co., USA). Samples for TEM measurements were deposited on copper grids. XRD patterns were recorded on a German Bruker AXS D8 ADVANCE X-ray diffractometer. The products were 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  $\text{cm}^{-1}$ . The samples were prepared in pellet form with spectroscopic-grade KBr.  $\text{N}_2$  adsorption-desorption measurements were conducted using Thermo Sorptomatic 1990 by  $\text{N}_2$  physisorption at 77 K. The as-calcined samples were out gassed for 4 h at 250 °C and the drug loaded samples were out gassed for 4 h at 80 °C under vacuum ( $p < 10^{-2}$  Pa) in the degas port of the sorption analyzer. The BET specific surface area of samples was 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.

*Catalytic Test:*  $\text{NaBH}_4$  reduction of 4NP catalyzed by  $\text{PS@PANI@Au/m-SiO}_2$  yolk/shell nanostructures: Typically, aqueous solution of  $\text{NaBH}_4$  (1.0 mL,  $1.5 \times 10^{-2}$  M) was mixed with aqueous 4NP 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

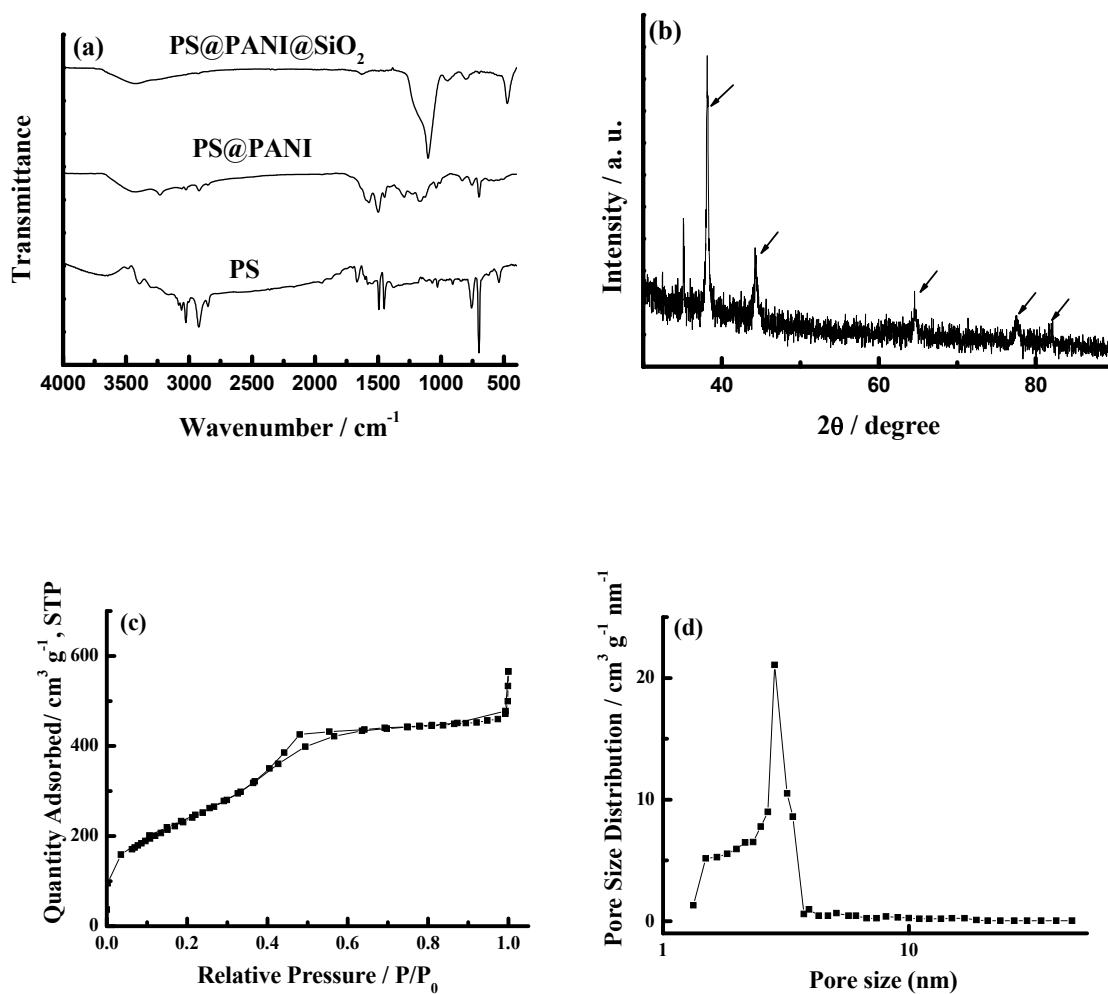
quickly placed in the cell holder of the spectrophotometer. The progress of the conversion of 4NP to 4AP was then monitored via the Uv-vis spectroscopy by recording the time-dependent adsorption spectra of the reaction mixture with a time interval of 10 min in a scanning range of 200-700 nm at ambient temperature.



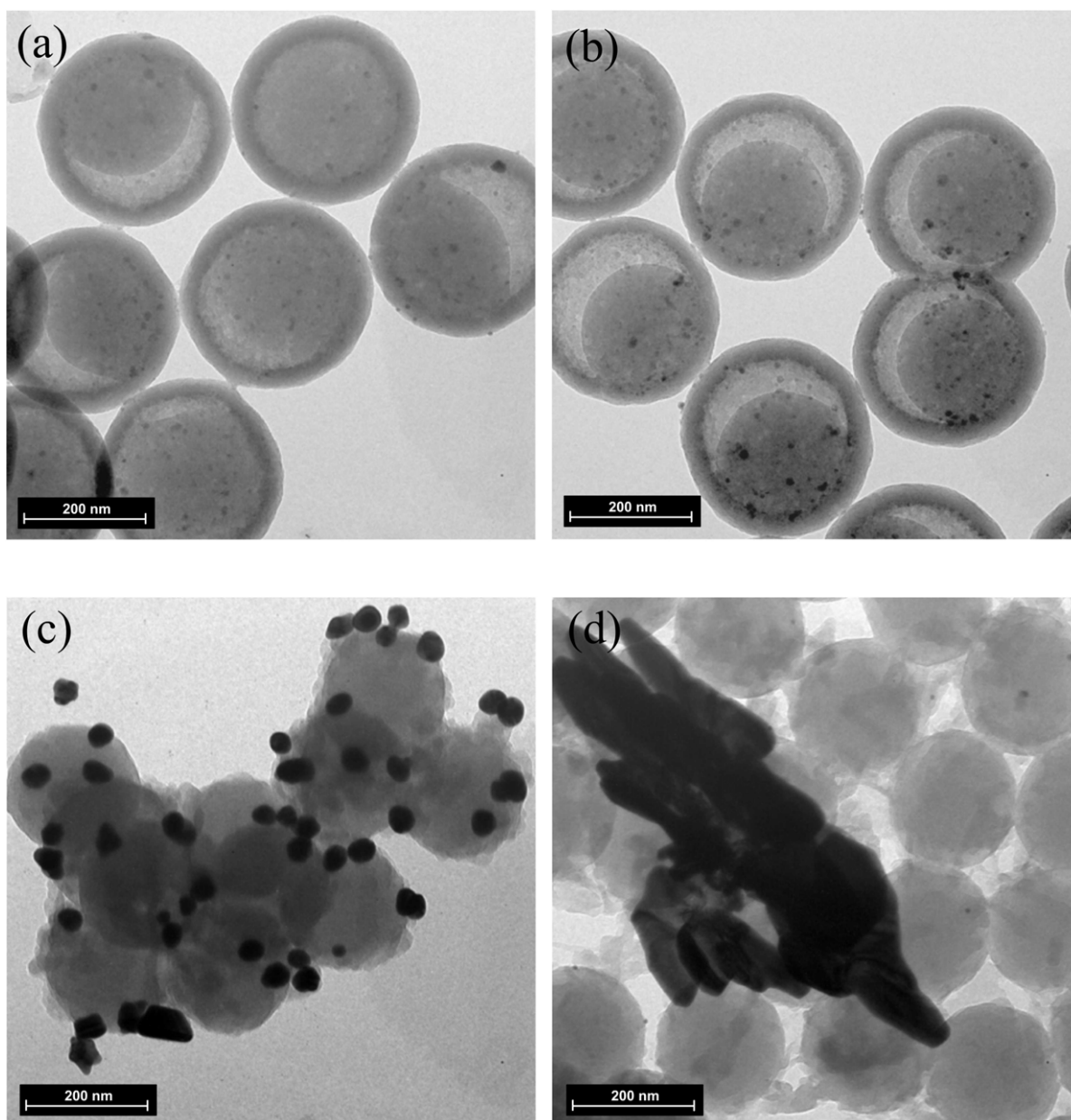
**Fig. S1** TEM images of (a) sulfonated PS nanospheres, (b) PS@PANI core@shell nanostructures, (c) PS@PANI@SiO<sub>2</sub> sandwich-like core@shell nanostructures and (d) PS@PANI/m-SiO<sub>2</sub> yolk/shell nanostructures.



**Fig. S2** Optical images of (a) PS, (b) PS@PANI, (c) PS@PANI/m-SiO<sub>2</sub>, and (d) PS@PANI@Au/m-SiO<sub>2</sub> colloids.

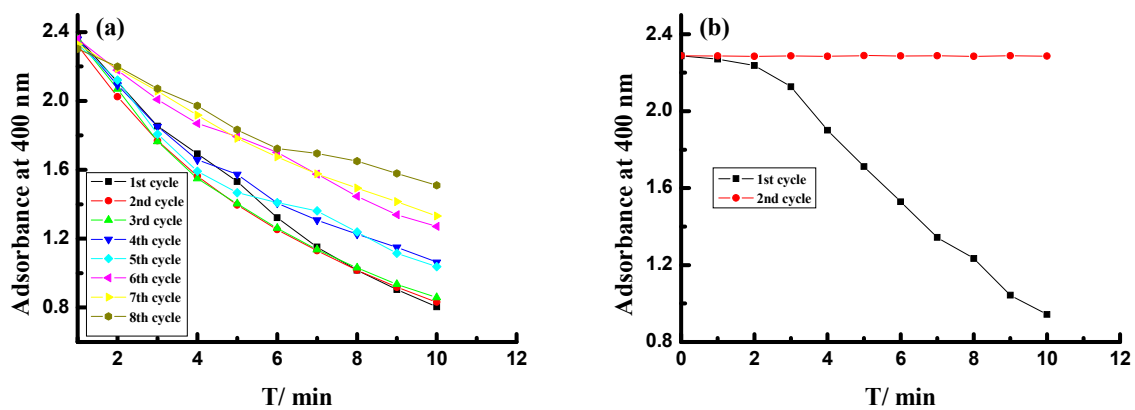


**Fig. S3** (a) FTIR spectra of PS, PS@PANI, and PS@PANI@SiO<sub>2</sub> nanostructures. (b) Wide-angle XRD patterns of PS@PANI@Au/m-SiO<sub>2</sub> yolk/shell nanostructures. (c) N<sub>2</sub> adsorption-desorption isotherm and (d) BJH pore size distribution of PS@PANI@/m-SiO<sub>2</sub> yolk/shell nanostructures displayed in Fig. S1d.



**Fig. S4** TEM images of (a, b) PS@PANI@Au/m-SiO<sub>2</sub> yolk/shell catalysts and (c, d) PS@PANI@Au catalysts (a, c) before and (b, d) after catalytic reaction.





**Fig. S5** (a) Adsorbance at the peak position for 4-NP (400 nm) as a function of time in the presence of (a) PS@PANI@Au/m-SiO<sub>2</sub> yolk/shell and (b) PS@PANI@Au catalysts.

**Tab. S1**  $k_{app}$  in different cycles of catalytic reduction of 4-NP in the presence of NaBH<sub>4</sub> with PS@PANI@Au/m-SiO<sub>2</sub> yolk/shell catalysts (Gold size: 5 nm).

Use	1st	2nd	3rd	4th	5th	6th	7th	8th
$k_{app}$ (min <sup>-1</sup> )	0.12	0.11	0.11	0.08	0.08	0.07	0.06	0.05

## References

- (1) Yang, Z. Z.; Li, D.; Rong, J. H.; Yan, W. D.; Niu, Z. W. *Macromol. Mater. Eng.* **2002**, 287, 627-633.