Electronic Supporting Information

Biogenic silver nanoparticles impregnated hollow mesoporous silicalite-1: An efficient catalyst for p-nitrophenol reduction

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Experimental section

For the synthesis of parent silicalite-1, 8.3 ml tetraethyl orthosilicate (TEOS) was added into a mixed solvent of 24.7 g DI water and 8.6 mL ethanol (C_2H_5OH) followed by dropwise addition of 7.4 mL 1 M tetrapropyl ammonium hydroxide (TPAOH) under stirring. The molar composition of the solution was maintained as $1SiO_2$: 0.2TPAOH: 4 C_2H_5OH: 46H_2O. After stirring for 6 h at room temperature, it was heated in an autoclave at 170°C/72h. The resulting solid was recovered by centrifugation, washing with DI water, and dried overnight at 100°C. Finally, the template (TPAOH) was removed by calcination at 550°C/6h.

For the synthesis of hollow silicalite-1, 4 g of calcined parent silicalite-1 was well dispersed in 40 mL 0.2 M TPAOH solution. The mixture was heated in an autoclave at 170°C/72h. Then the resulting product was recovered by centrifugation, washing with DI water, and dried overnight at 100°C. Finally, the template was removed by calcination at 550°C/6h.

For the synthesis of AgNPs impregnated hollow silicalite-1, 0.068 g of hollow silicalite-1 powder was dispersed in 50 mL DI water under ultrasonication followed by dissolving 0.034 g (0.2 mmol) $AgNO_3$. 10 mL of *carambola* fruit extract was added into

the above disperson followed by dropwise addition of 1M NaOH under stirring to maintain the pH 10. The whole reaction mixture was kept in dark under constant stirring for 12 h. The obtained product was then separated by centrifugation, washed with DI water for several times and finally with ethanol to remove the biomolecules. It was then dried in air at room temperature.

Characterization

Powder X-ray diffraction (PXRD) studies of the samples were performed by Philips X'Pert Pro PW 3050/60 powder diffractometer using Ni-filtered Cu-Kα radiation (λ = 0.15418 nm) operated at 40 kV and 30 mA. The characteristic vibration bands of the products were confirmed by FTIR (Nicolet-380, Thermo Electron Corporation, USA) with KBr pellet at a resolution of 4 cm-1. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI 5000 Versaprobe II Scanning XPS microprobe (ULVAC-PHI, USA). The spectra were recorded with monochromatic AlKα (hν = 1486.6 eV) radiation with an overall energy resolution of ~0.7 eV. Nitrogen adsorption-desorption measurements were conducted at 77 K with a Quantachrome (ASIQ MP) instrument. The surface area was obtained using Brunauer-Emmet-Teller (BET) method and the pore size distributions were calculated by Barret-Joyner-Halenda (BJH) method and density functional theory (DFT) method. The nitrogen adsorption volume at the relative pressure (P/Po) of 0.99 was used to determine the pore volume. The morphology of the particles was examined by FESEM (Model: Zeiss, SupraTM 35VP, Germany) operating with an accelerating voltage of 10 kV, and TEM using a Tecnai G2 30ST (FEI) instrument operating at 300 kV. Elemental composition of the sample was analyzed with energy

dispersive analysis of X-ray spectroscopy (EDS) coupled to TEM. UV–Visible spectra were recorded using UV-VIS-NIR spectrophotometer (UV-3101PC, Shimadzu) in the wavelength range of 200 nm to 600 nm.

Catalytic performance

To study the catalytic activity of AgNPs impregnated silicalite-1, 1 mg of the catalyst was placed in a reaction mixture containing 4-NP (0.1 mL; 3.0 x 10-3 M), water (2.8 mL), NaBH4 (0.1 mL; 3.0 x 10-1 M) solutions in the cuvette cell. The molar ratio of 4-NP: NaBH4 was 1:100. The UV-Vis spectral changes were monitored at different time intervals using UV-visible-NIR spectrophotometer (V-730/730 BIO, JASCO) in the wavelength range of 200 nm to 600 nm. To reuse the catalyst, it was washed with DI water and dried at room temperature. Then the catalyst was ready to use for next time. The kinetics of the reaction is represented by lnAt/Ao = -kt, where, k is pseudo first order rate constant, t is the reaction time, Ao is the concentration of 4-NP at time t = 0, and At is the concentration of the same at time t.

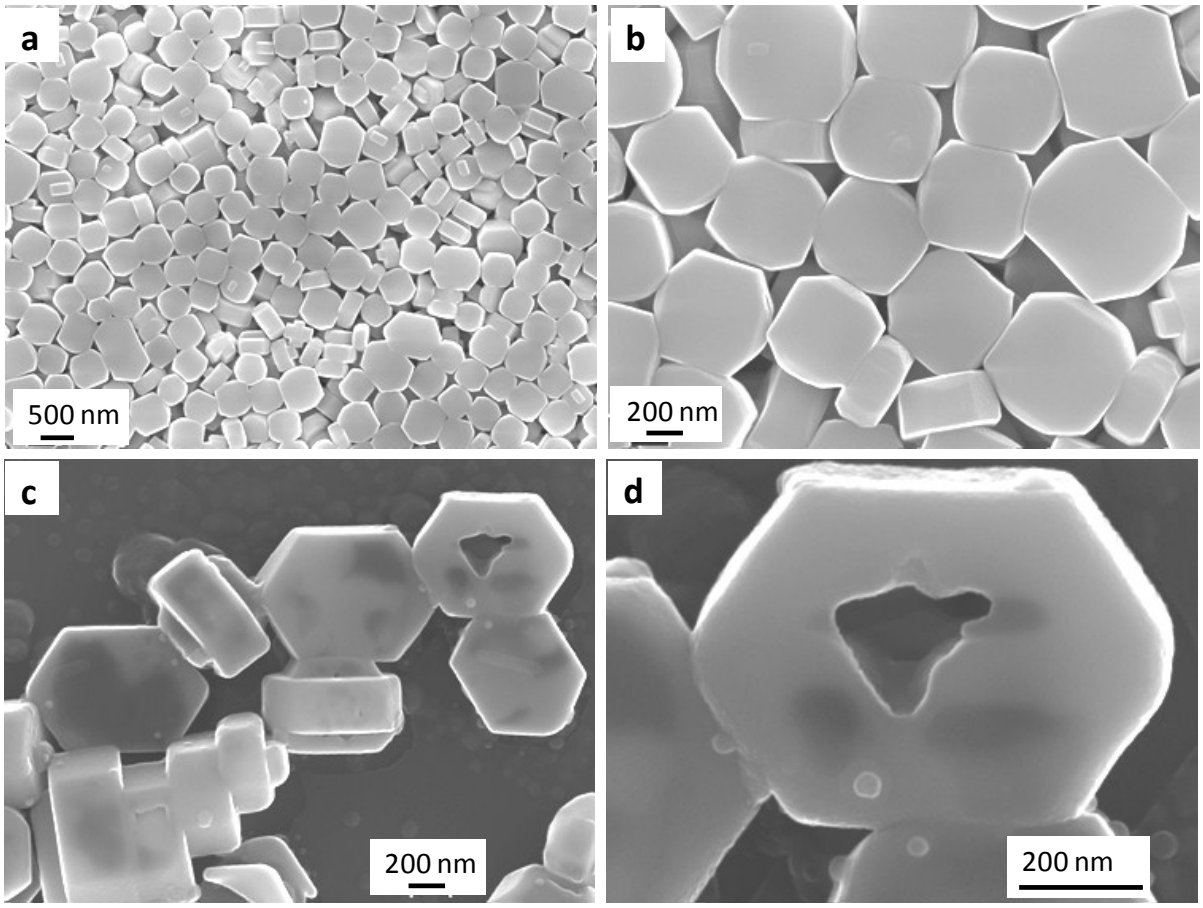

Fig. S1: FESEM images of (a,b) parent silicalite-1 particles, and (c,d) hollow silicalite-1 after alkali treatment

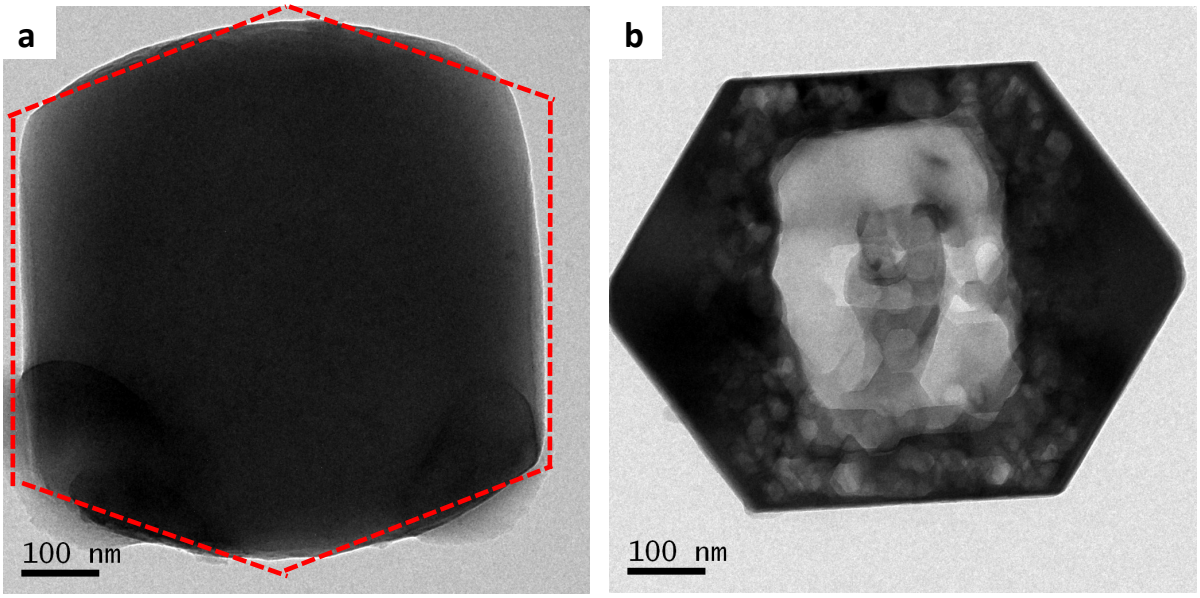

Fig. S2: TEM images of (a) parent silicalite-1 particles, and (b) hollow silicalite-1 after alkali treatment

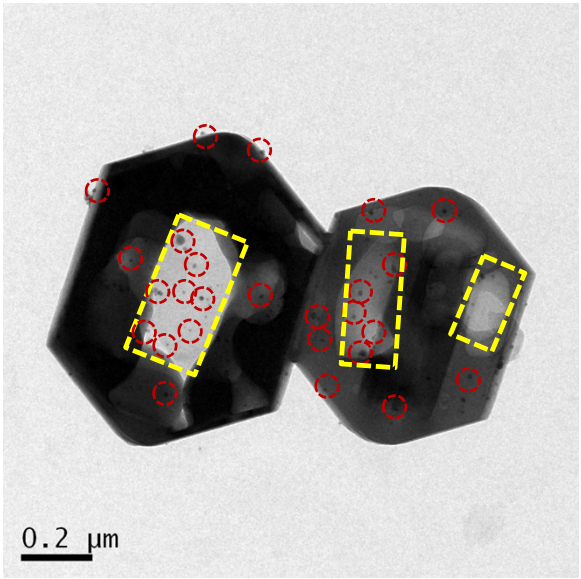

Fig. S3: TEM image of Ag impregnated hollow silicalite-1 particles with thicker shell

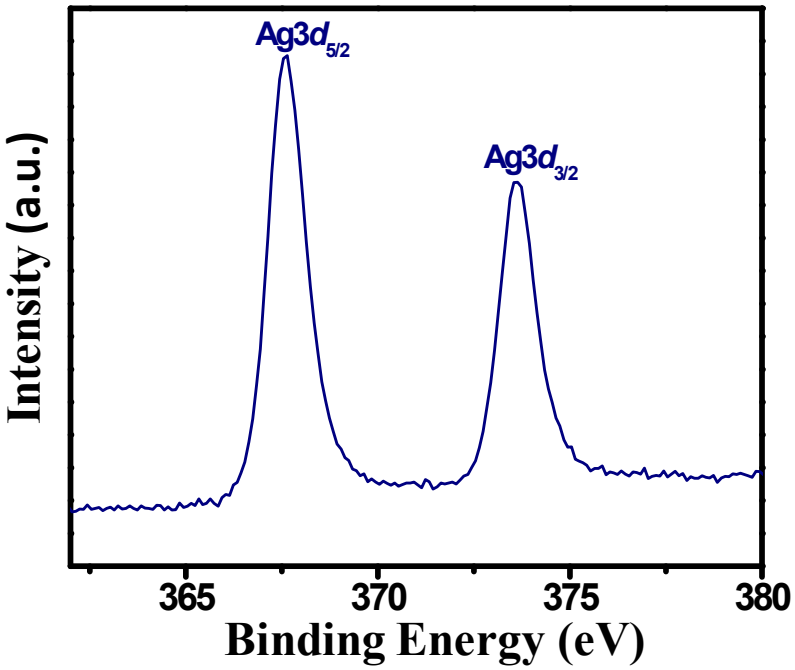

Fig. S4: X-ray photoelectron spectroscopy of Ag in AgNPs impregnated hollow silicalite-1

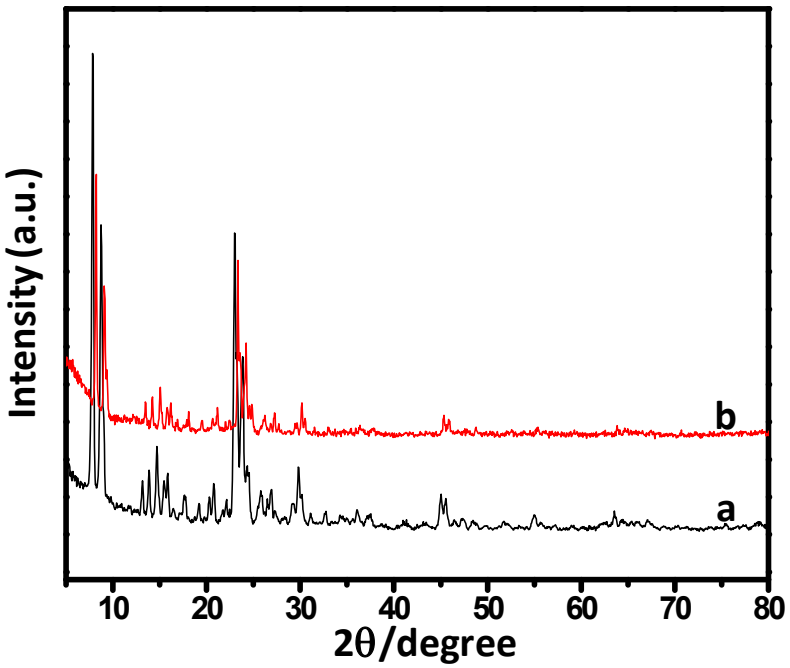

Fig. S5: XRD patterns of (a) parent silicalite-1 and (b) hollow silicalite-1

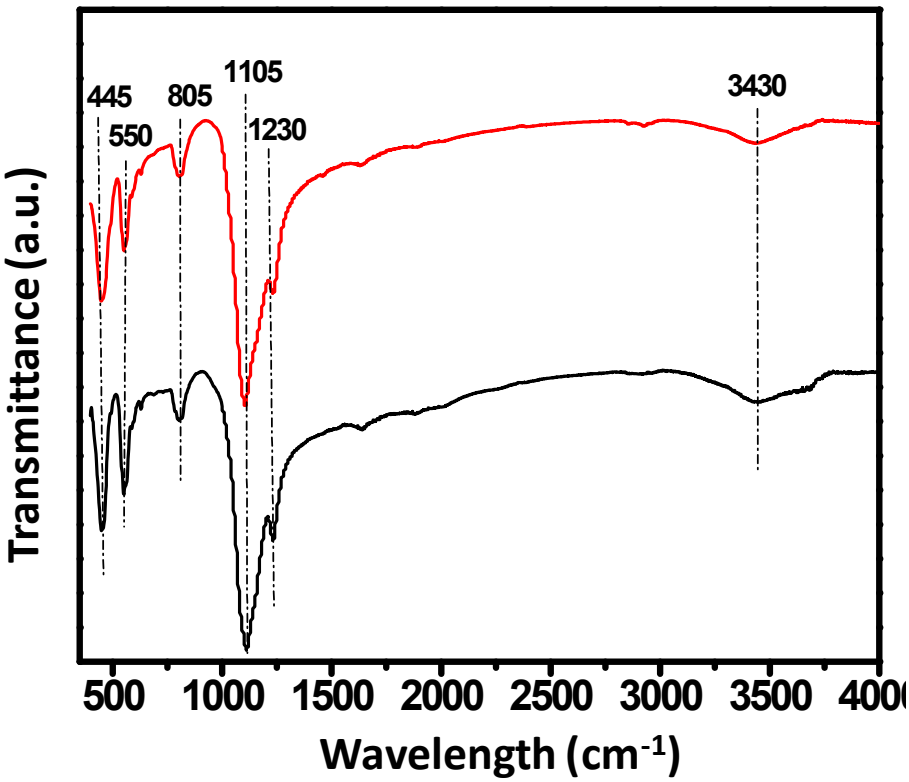

Fig. S6: XRD patterns of (a) parent silicalite-1 and (b) hollow silicalite-1

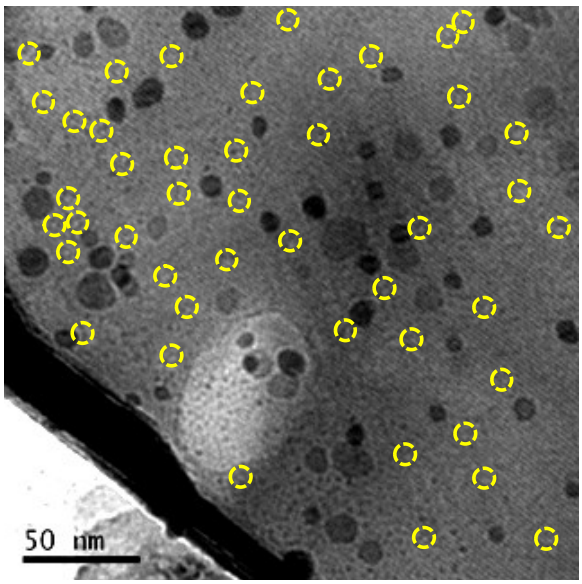

Fig. S7: TEM image of Ag impregnated hollow silicalite-1 showing mesoporosity (circle mark) in the sample

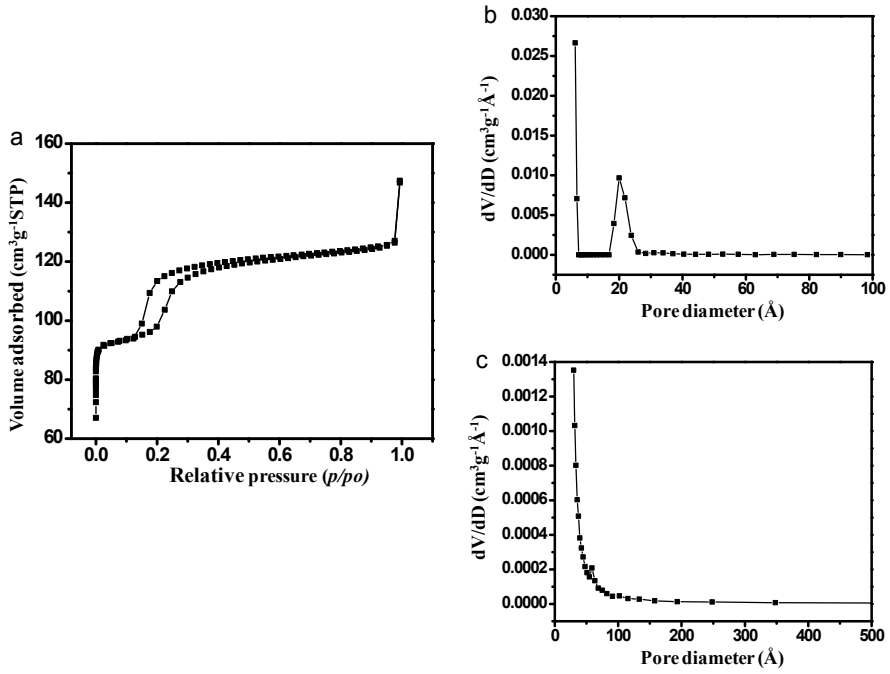

Fig. S8: (a) N_2 adsorption-desorption isotherms, and pore size distributions (PSD) by (b) DFT and (c) BJH methods of parent silicalite-1 particles.

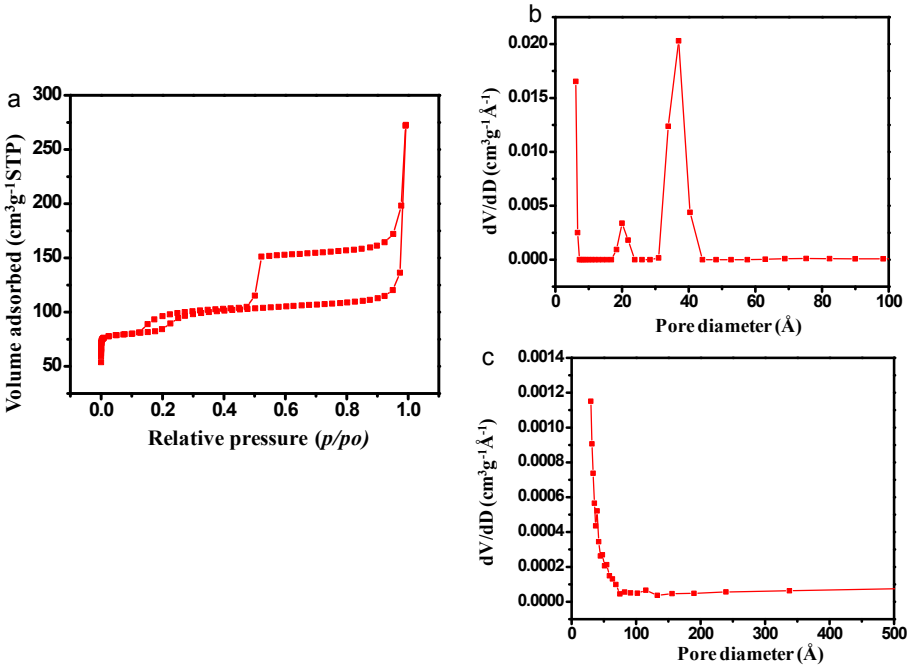

Fig. S9: (a) N_2 adsorption-desorption isotherms, and pore size distributions (PSD) by (b) DFT and (c) BJH methods of hollow silicalite-1 particles.

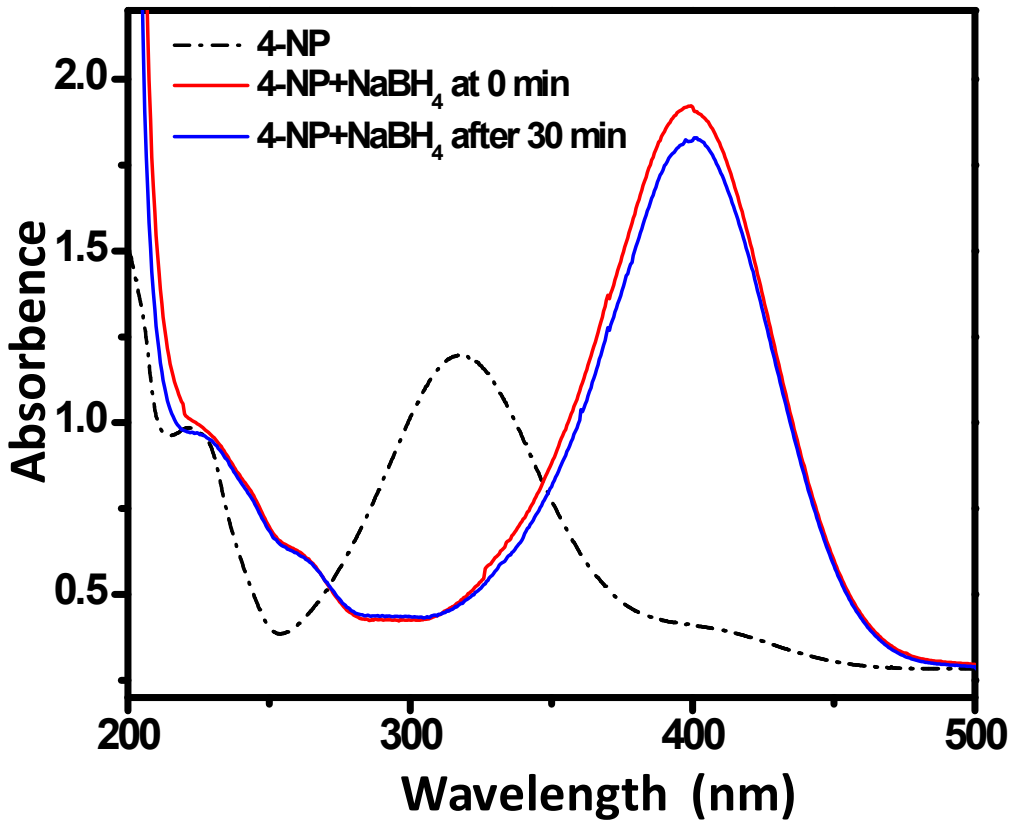

Fig. S10: The UV-Vis absorption of 4-NP, 4-NP+$NaBH_4$ (at 0 min) and 4-NP+NaBH4 (after 30 min)

Table S1. Comparison of rate constant (k) and activity parameter (κ) of AgNP catalysts for PNP reduction.

Nanoparticles	k (s^{-1})	κ ($s^{-1}g^{-1}$)*	References
AgNP aggregates	2.1×10^{-3}	2.0	26
AgNP spherical	3.64×10^{-4}	0.09	27
Ag dendrite (coral like)	5.19×10^{-3}	1.30	27
Ag dendrite (banana leaf like)	1.65×10^{-3}	0.41	27
Ag-C	1.69×10^{-3}	1.69	28
Biogenic AgNP	4.06×10^{-3}	-----	29
Biogenic Ag impregnated hollow silicalite-1	5.5×10^{-3}	65.63	this work

*Rate constant per unit mass of Ag.