Electronic Supplementary Information

Cauliflower-like hierarchical silicalite-1 supported AuNPs toward improved catalytic reduction of *p*-nitrophenol

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Experimental Section

Synthesis of cauliflower-like hierarchical silicalite-1

For the synthesis of cauliflower-like hierarchical silicalite-1, 3 g P(AAm-co-DADMAC) was mixed with 24.7 mL H_2O and 8.6 mL ethanol under stirring. 8.3 mL of TEOS (tetraethyl orthosilicate) was added dropwise to the mixture at room temperature (30°C), and stirring was continued for 1 h. Then 7.4 mL of TPAOH (tetrapropyl ammonium hydroxide) was added slowly into the solution, and kept at 40 °C under stirring to obtain a gel mass. The molar composition of the solution was maintained as $1SiO_2$: 0.2TPAOH: $46H_2O$. It was heated in an oven at 100°C for 12h. 0.5 g of the resulting dry gel mass was put into a Teflon cup (support) placed in a Teflon-lined autoclave (100 mL) filled with 40 mL of water where the dry gel mass was not in direct contact of water (shown in Fig. S1). The autoclave containing dry gel mass and water was sealed and hydrothermally treated at 150 °C for 72 h. In this process the evaporated water (steam) takes part for the crystallization. After the steam-assisted synthesis, the obtained material was dried at 100 °C overnight followed by calcination at 550 °C/6 h. The sample is designated as PSAZ-550.

Preparation of AuNPs impregnated cauliflower-like hierarchical silicalite-1

For impregnation of AuNPs in cauliflower-like silicalite-1, 1g of prepared silicalite-1 was dispersed in 50 mL of water followed by the addition of 0.023 g of $HAuCl_4$ (1.2 wt% Au) under stirring for 1h. Subsequently, freshly prepared 20 mL sodium borohydride ($NaBH_4$) (0.2 mmol) solution was added dropwise into the reaction mixture under vigorous stirring in ice-bath, and stirring was continued for 1 h. During the reaction, color of the solution slowly turned into black indicating the formation of AuNPs. Then it was centrifuged at 10000 rpm followed by drying at 100 °C/10h. The sample is designated as Au-PSAZ-550.

Catalytic study

The catalytic reduction of *p*-nitrophenol (4-NP) with AuNP impregnated cauliflower-like hierarchical silicalite-1 (Au-PSAZ-550) was carried out in the presence excess $NaBH_4$. In this process different amounts of catalyst were introduced in a reaction mixture containing 0.1 mL 4-NP *(*3.0×10^{-3} M), 0.1 mL $NaBH_4$ (3.0 x 10–1 M) and 2.8 mL water at 25 °C in a standard quartz cuvette cell. The molar ratio of 4-NP: $NaBH_4$ was 1:100. The progress of the reaction (i.e. the reduction of 4-NP to 4-AP) was monitored at different time intervals using UV-Vis spectrophotometer (Jasco V-730) in the wavelength range of 200 to 500 nm. The apparent rate constant (k) was evaluated by the extinction of the solution at 400 nm (absorption of *p*-nitrophenolate ion). To reuse the catalyst, the catalyst was washed with DI water and dried at room temperature. To optimize the amount of catalyst, it was varied in the range of 1-3 mg. The reaction kinetics using the catalyst is represented by $\ln A_t/A_o = -kt$, where, k is pseudo-first order rate constant, t is the reaction time, A_o is the concentration of 4-NP at time t = 0, and A_t is the concentration of the same at time t.

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-K_α radiation (λ = 0.15418 nm) operated at 40 kV and 30 mA. 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 AlK_α ($h\nu$ = 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-Emmett-Teller (BET) method and the pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) method and density functional theory (DFT) method. The nitrogen adsorption volume at the relative pressure (p/p_o) of 0.99 was used to determine the pore volume. The morphology of the particles was examined by FESEM (Model: Zeiss, Supra^{TM} 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. Elemental analysis for Au in silicalite-1 was carried out by ICP-AES (inductively coupled plasma atomic emission spectroscopy, Model: Spectro Ciros Vision, Germany). UV–Visible spectra were recorded using UV-Vis spectrophotometer (Jasco V-730) in the wavelength range of 200 to 500 nm.

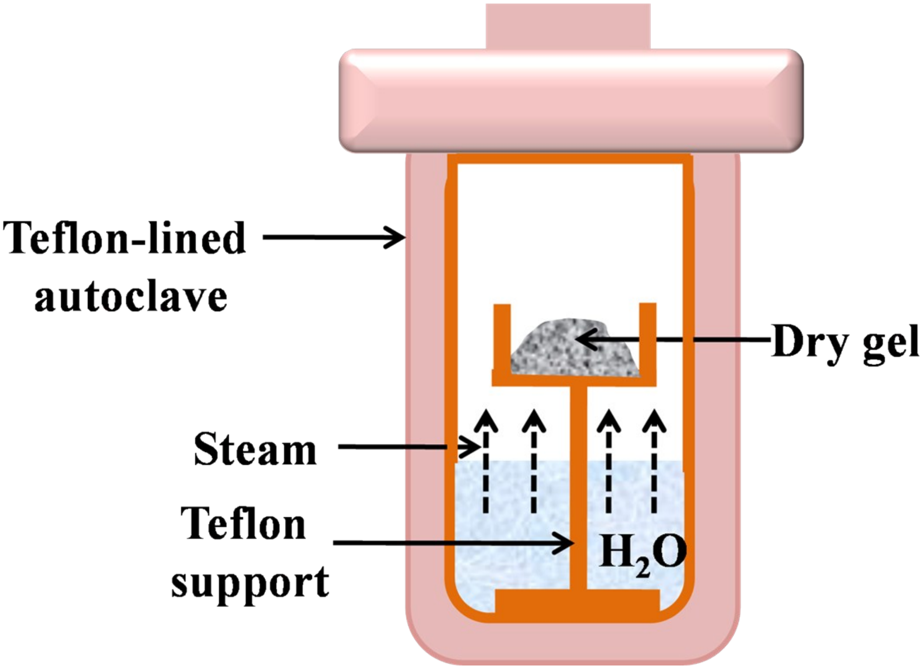

Fig. S1: Steam-assisted crystallization (SAC) in a Teflon-lined stainless steel autoclave

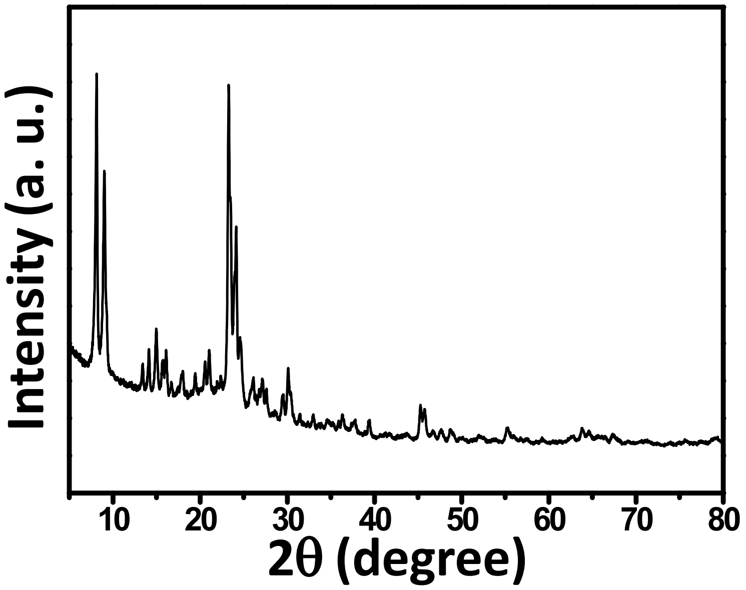

Fig. S2: XRD pattern of PSAZ-550 synthesized using P(AAm-co-DADMAC) *via* SAC method in the absence of AuNPs.

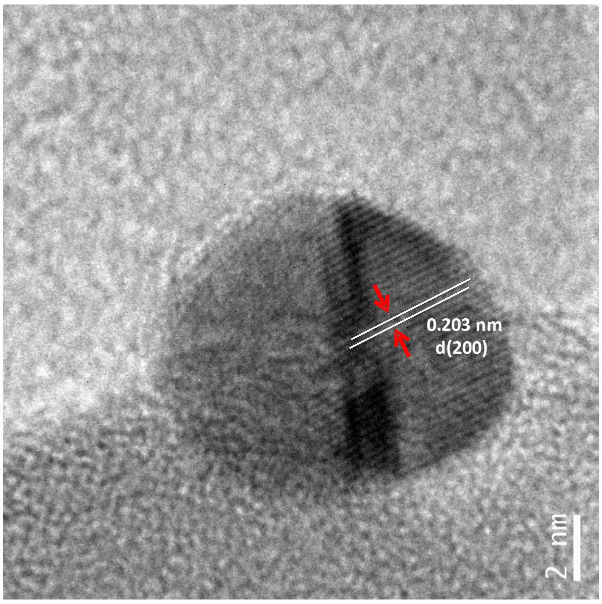

Fig. S3: TEM image of AuNP embedded in silicalite-1 wall

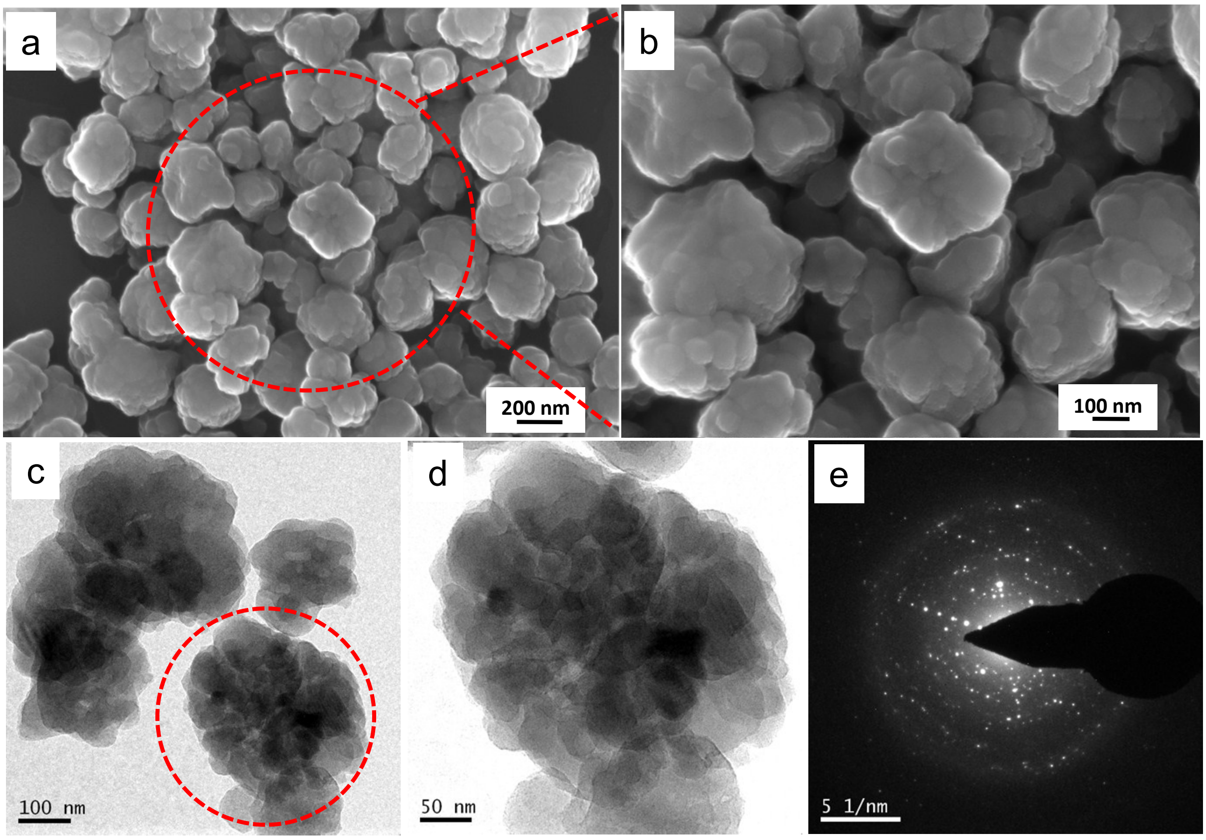

Fig. S4: (a,b) FESEM, (c,d) TEM images and (e) SAED pattern of PSAZ-550 synthesized using P(AAm-co-DADMAC) *via* SAC method in the absence of AuNPs.

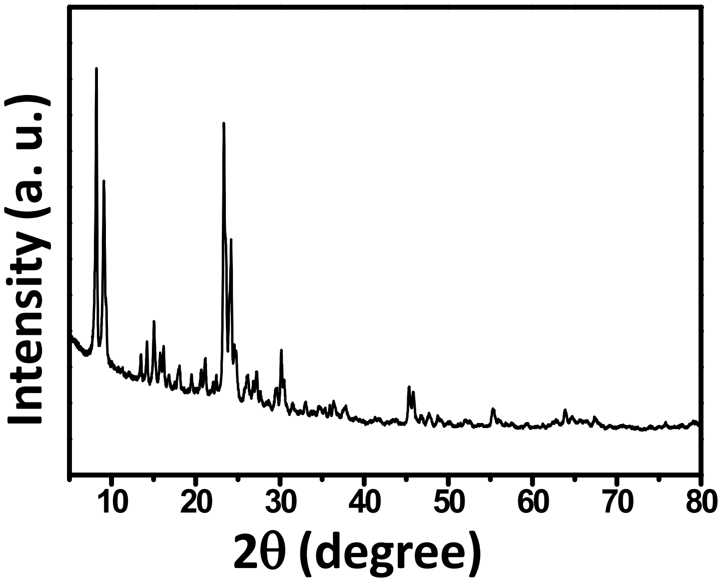

Fig. S5: XRD patterns of SAZ-550 synthesized without using P(AAm-co-DADMAC) *via* SAC method.

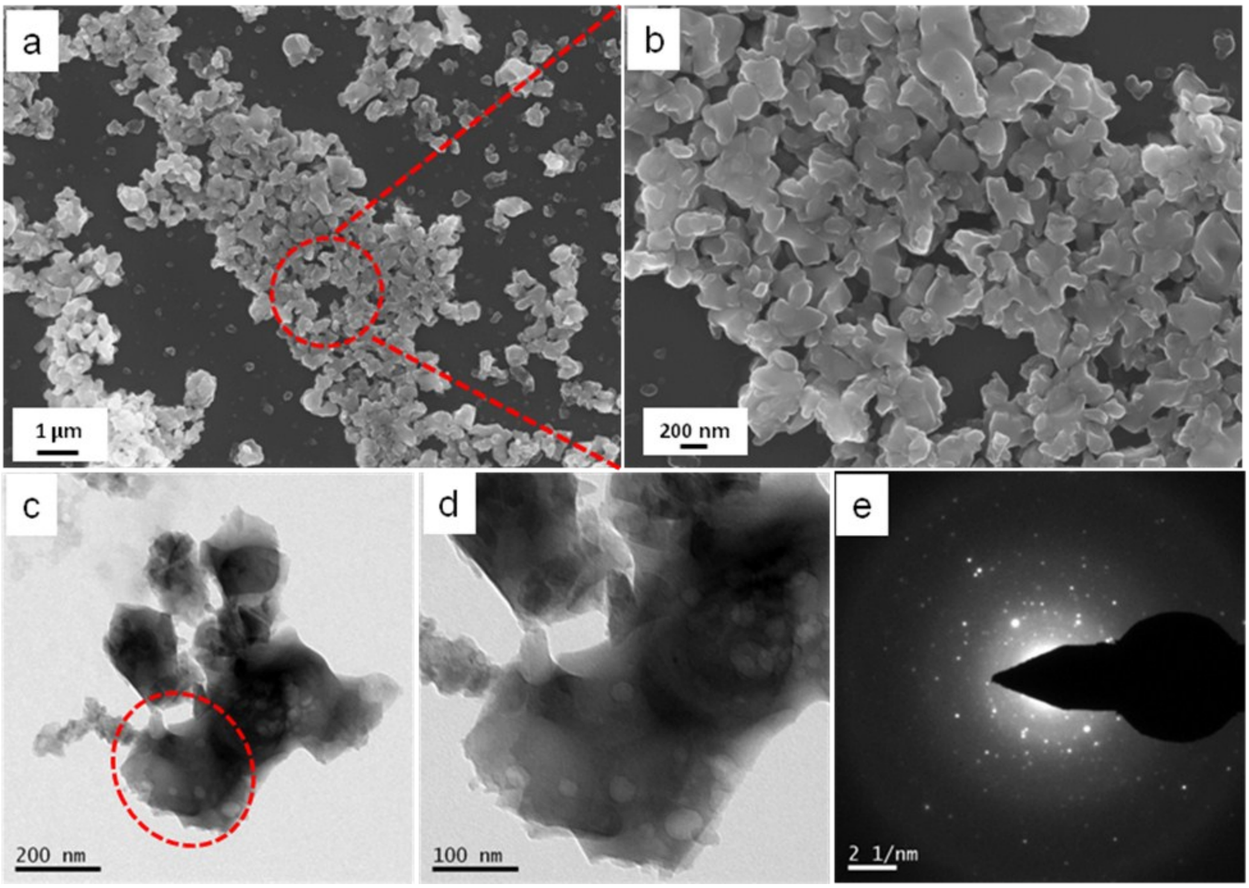

Fig. S6: (a,b) FESEM, (c,d) TEM images and (e) SAED pattern of SAZ-550 synthesized without using P(AAm-co-DADMAC) *via* SAC method.

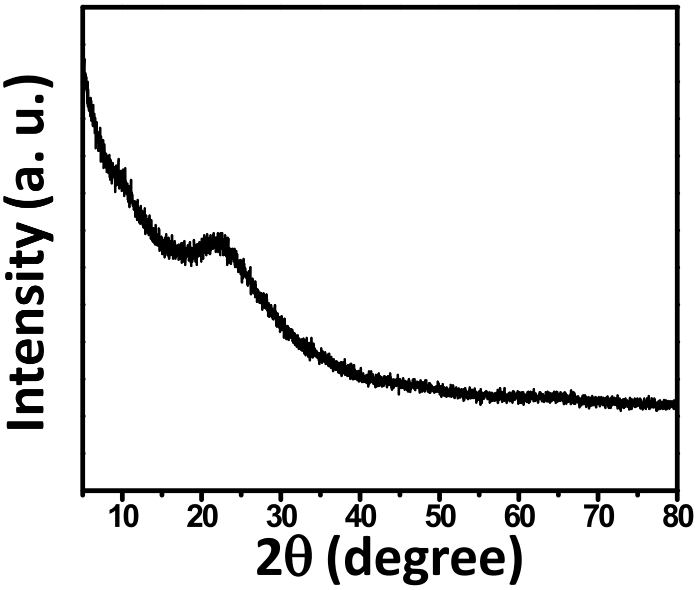

Fig. S7: XRD patterns of the calcined sample (PS-550) prepared in the presence of P(AAm-co-DADMAC) prior to SAC process.

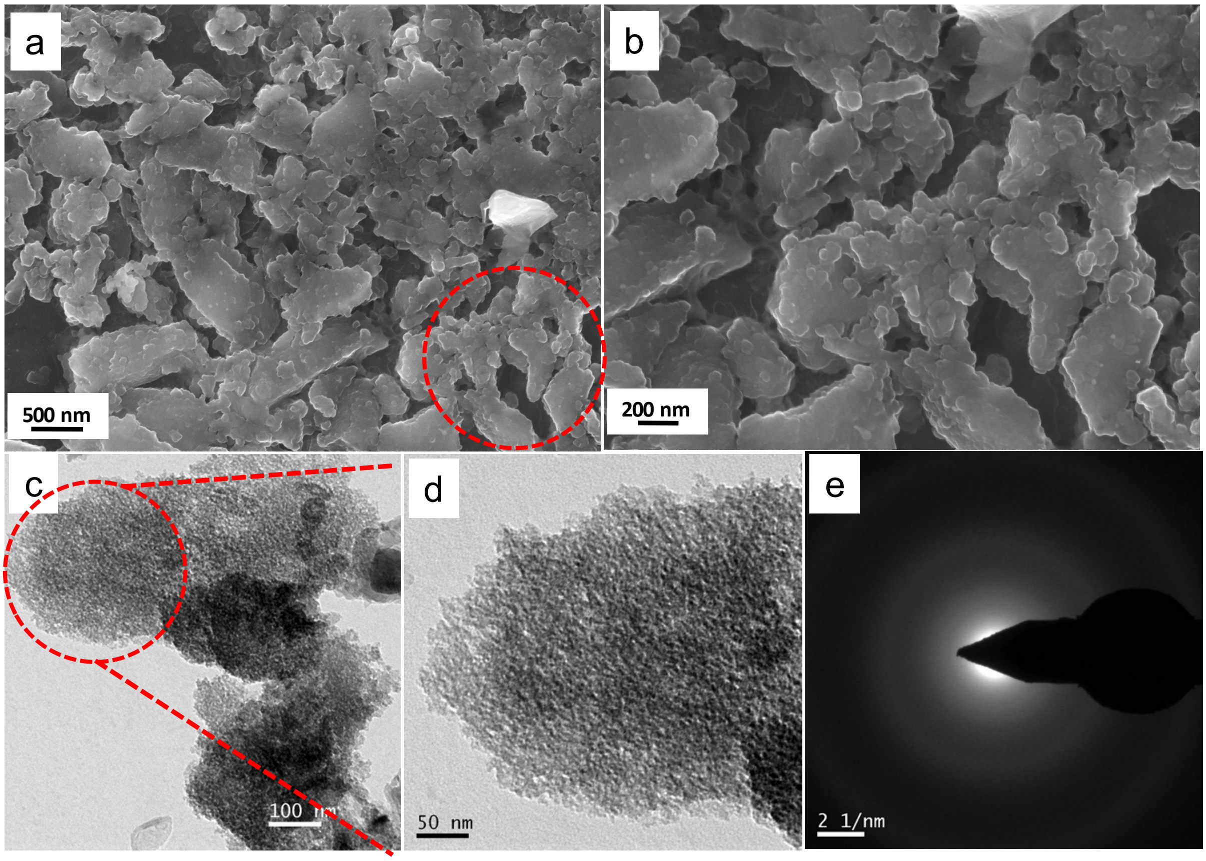

Fig. S8: (a,b) FESEM, (c,d) TEM images and (e) SAED pattern of the calcined sample (PS-550) prepared in the presence of P(AAm-co-DADMAC) prior to SAC process.

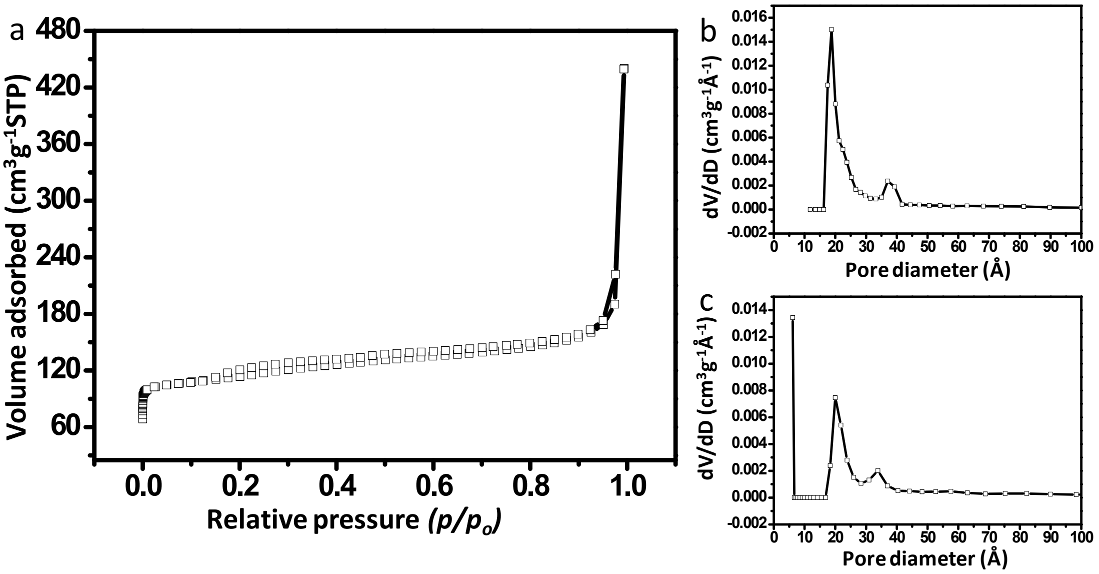

Fig. S9: (a) N_2 adsorption-desorption isotherm, pore size distributions (PSDs) by (b) BJH and (c) DFT method of PSAZ-550 synthesized using P(AAm-co-DADMAC) *via* SAC method in the absence of AuNPs.

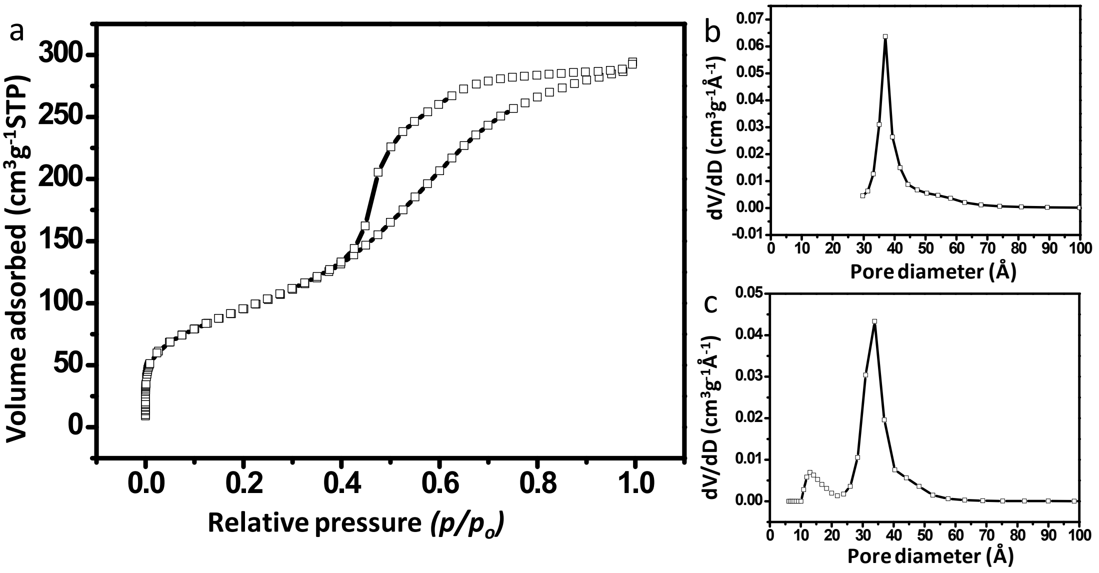

Fig. S10: (a) N_2 adsorption-desorption isotherms, pore size distributions (PSDs) by (b) BJH and (c) DFT method of the calcined sample (PS-550) prepared in the presence of P(AAm-co-DADMAC) prior to SAC process.

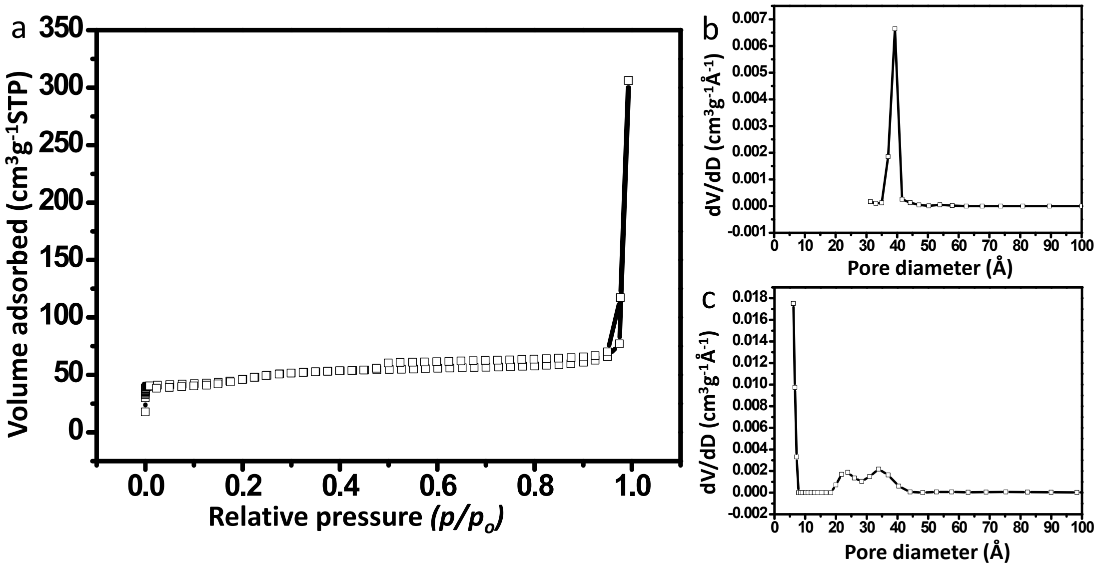

Fig. S11: (a) N_2 adsorption-desorption isotherm, pore size distributions (PSDs) by (b) BJH and (c) DFT method of SAZ-550 synthesized without using P(AAm-co-DADMAC) *via* SAC method.

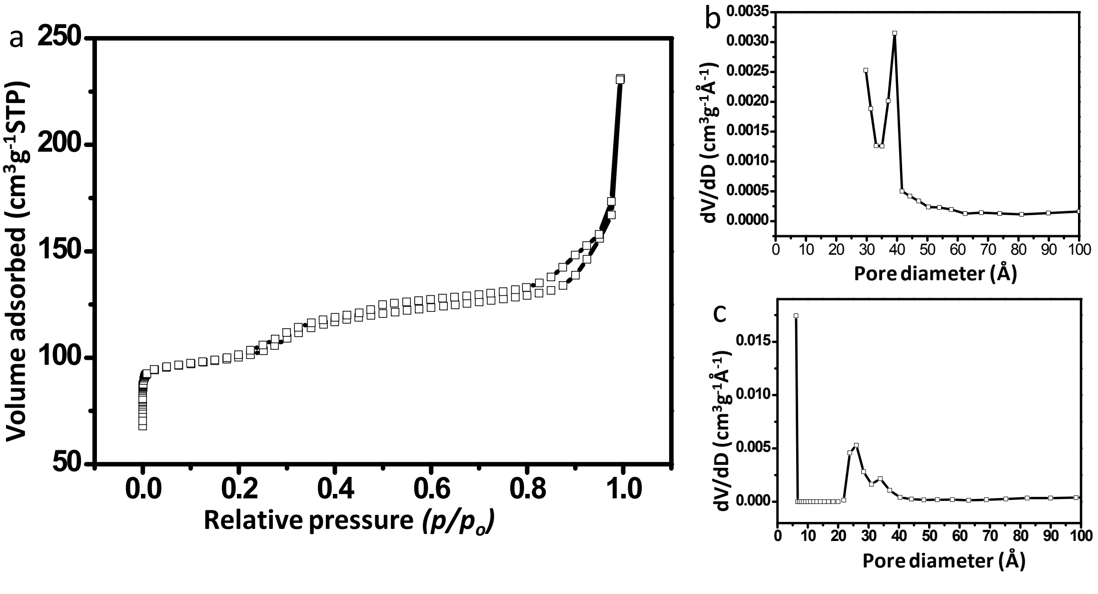

Fig. S12: (a) N_2 adsorption-desorption isotherm, pore size distributions (PSDs) by (b) BJH and (c) DFT method of silicalite-1 synthesized using P(AAm-co-DADMAC) *via* SAC method at 130 °C/72 h.

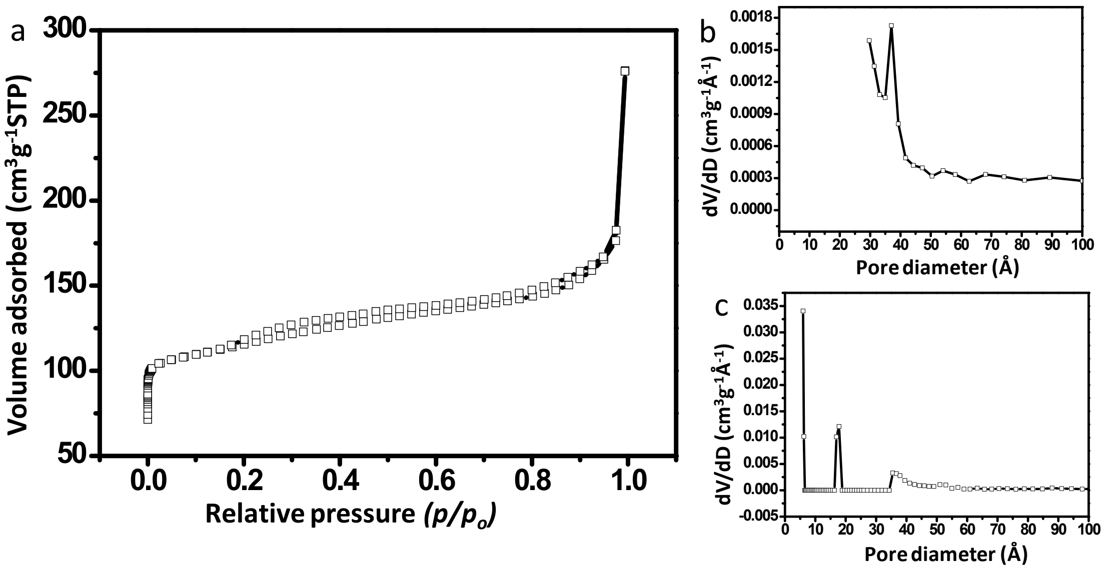

Fig. S13: (a) N_2 adsorption-desorption isotherm, pore size distributions (PSDs) by (b) BJH and (c) DFT method of silicalite-1 synthesized using P(AAm-co-DADMAC) *via* SAC method at 170 °C/72 h.

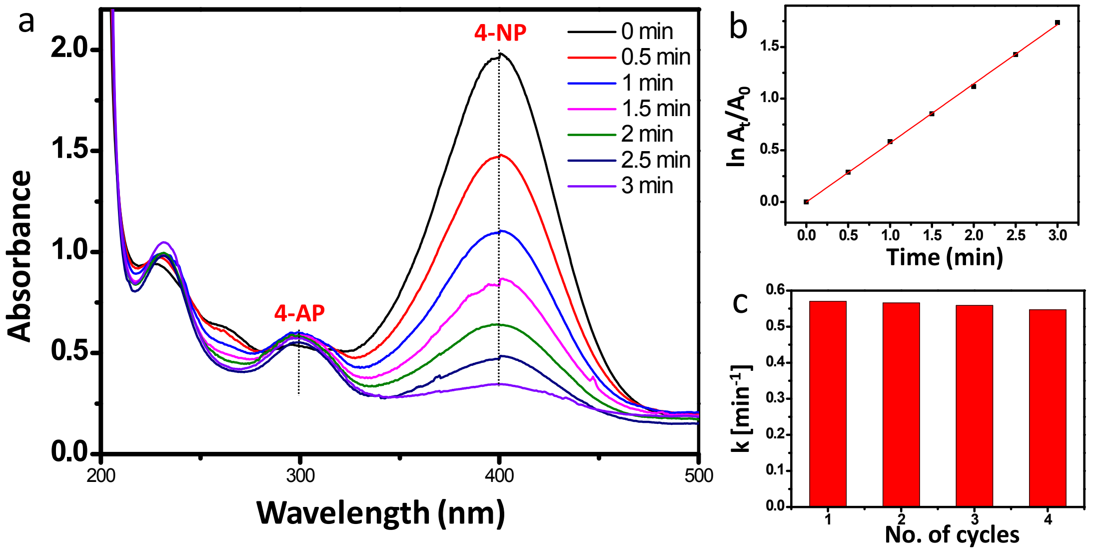

Fig. S14 : (a) UV –visible absorption spectra for the reduction of *p*-nitro phenol in the presence of 2 mg of Au-PSAZ-550 particles, (b) pseudo-first order plot of (-ln A_t/A_0) *vs.* reaction time for above reaction, (c) recyclability test.

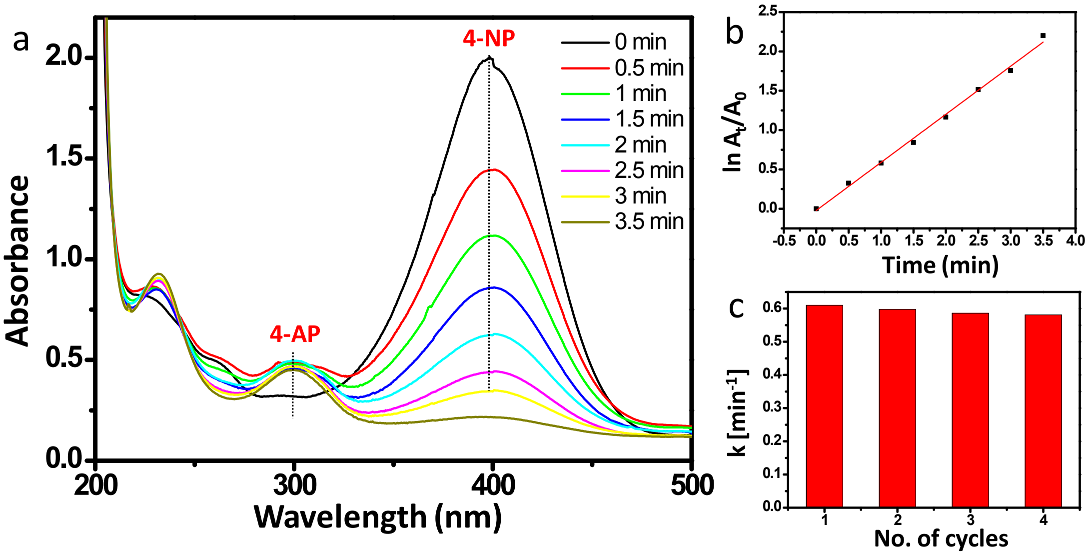

Fig. S15 : (a) UV –visible absorption spectra for the reduction of *p*-nitro phenol in the presence of 3 mg of Au-PSAZ-550 particles, (b) pseudo-first order plot of (-ln A_t/A_0) *vs.* reaction time for above reaction, (c) recyclability test.

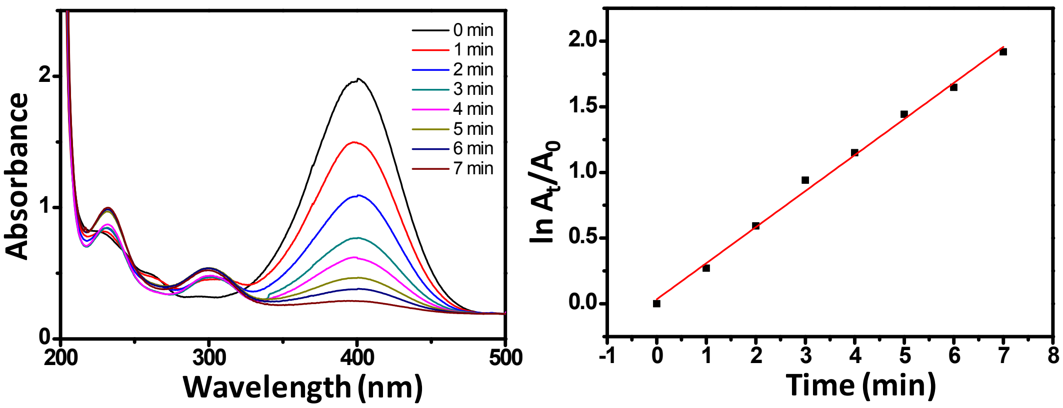

Fig. S16 : (a) UV–visible absorption spectra for the reduction of *p*-nitro phenol in the presence of 1 mg of Au-SAZ-550 synthesized without using P(AAm-co-DADMAC) *via* SAC method, (b) pseudo-first order plot of (-ln A_t/A_0) *vs.* reaction time for above reaction

Table S1: Textural properties of the sample PSAZ-550 synthesized at 130 °C and 170 °C for 72 h each

Synthesis Temperature (^oC)	S_{BET} (m^2g^{-1})[a]	$S_{Micropore}$ (m^2g^{-1})[b]	$S_{external}$ (m^2g^{-1})[c]	$V_{p\text{-}total}$ (cm^3g^{-1})[d]	d_P (Å)[e]
130	364	270	94	0.3575	39
170	416	310	106	0.4273	41

[a]BET surface area. [b]Micropore surface area. [c]External surface area. [d]Total pore volume. [e]Average pore size

Table S2: Time for completion of reaction, k, R^2 and κ for different amounts of catalyst.

Serial No	Amount of catalysts (mg)	Time (min)	k (s^{-1})	R^2	κ (s^{-1} g^{-1})
1	1	4	$7.7x\ 10^{-3}$	0.999	146.4
2	2	3	$9.5\ x\ 10^{-3}$	0.999	90.3
3	3	3.5	$10.1\ x\ 10^{-3}$	0.995	64.06