Supporting information

for

Core-Shell Au@AuAg Nano-Peanuts for the Catalytic Reduction of 4-Nitrophenol: Critical Role of Hollow Interior and Broken Shell Structure

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(1) <u>SEM images of the nanostructures.</u>

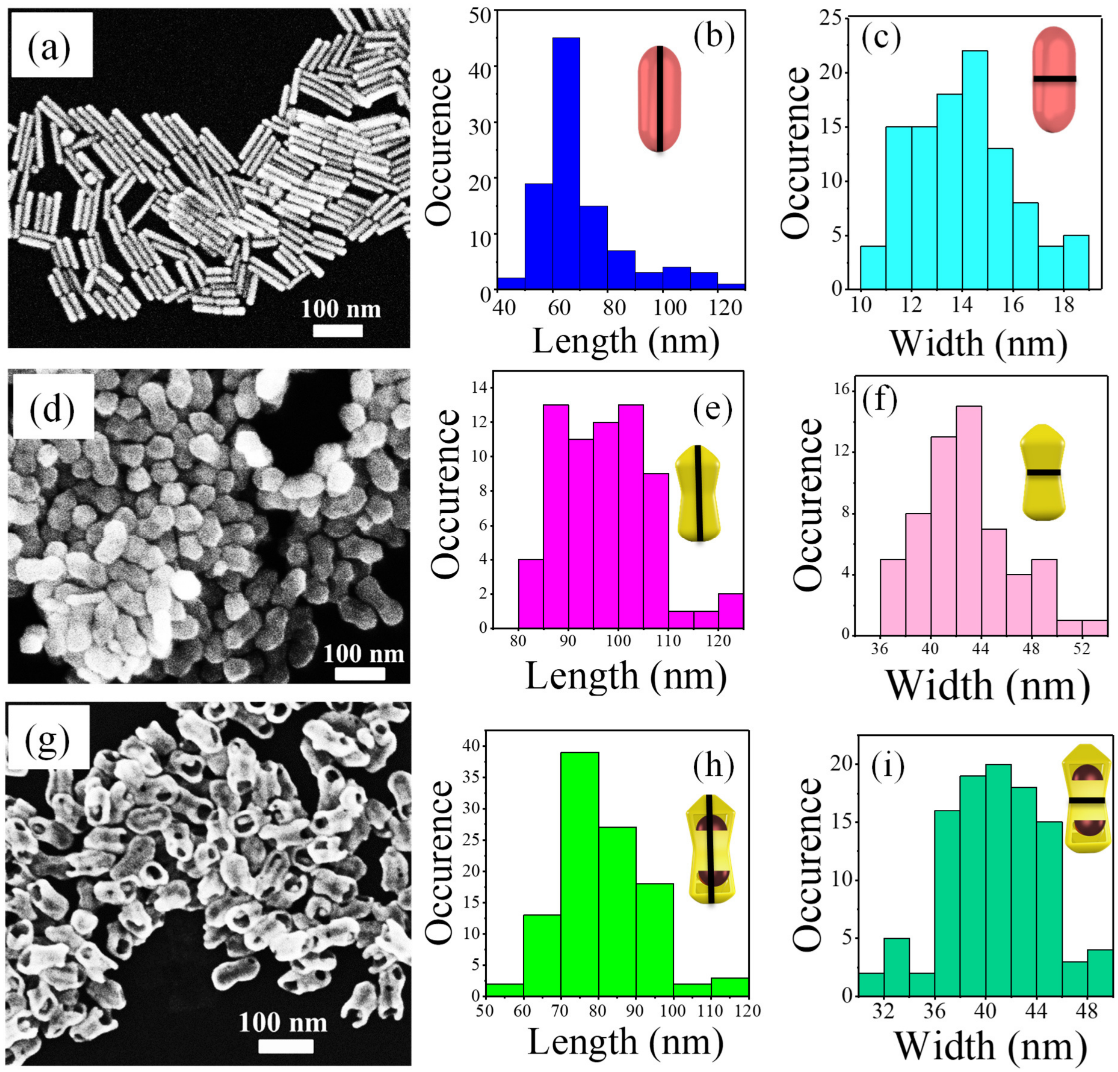

Figure S1: SEM images of the nanostructures with corresponding histogram distribution plot of length and width. (a) Nanorod with average length of 70.7±17 nm (b) and average width of 15±2 nm (c). (d) Peanut with average length of 97.2±9 nm (e)and width of 42.7±3 nm(f). (g) Broken shell peanut with average length of 81.3±12 nm (h) and average width of 40.8±3nm (i) The measured length and width of the NS are shown in black lines. From peanut to broken peanut formation, the tip leaches by ~16nm and side leaches by ~2nm.

(2) Characterization of the nanostructures through X-Ray Photo-electron Spectroscopy (XPS), Inductively coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Electron Dispersive X-Ray Spectroscopy (EDS).

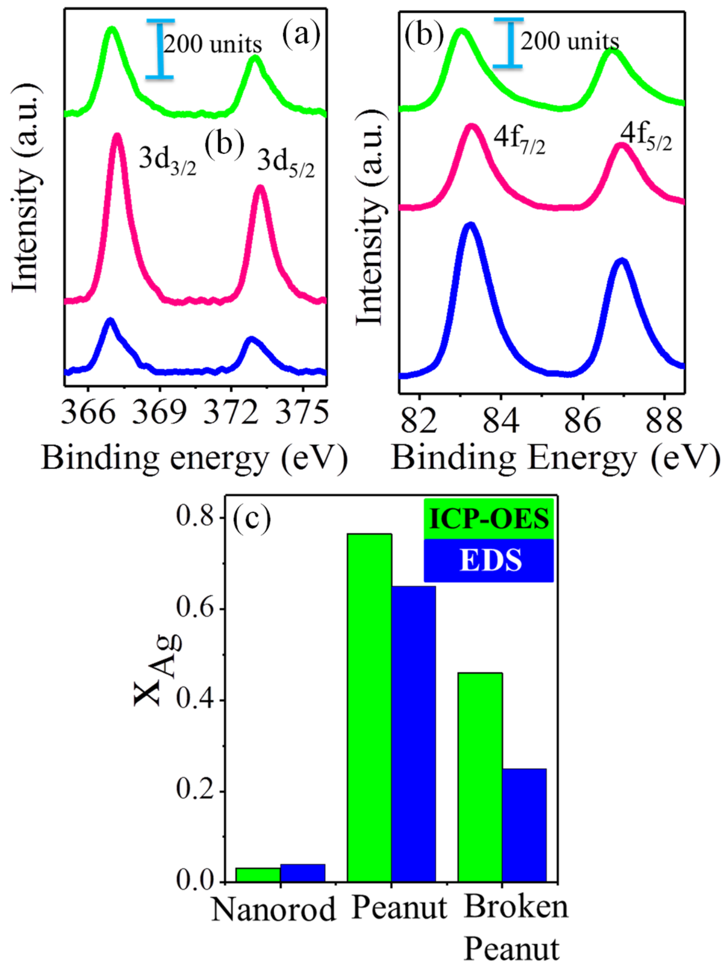

Figure S2: XPS spectra depicting the presence of (a) Ag and (b) Au in nanorod (blue), peanut (magenta) and broken shell peanut (green). (c) Molar ratio of [Ag] in nanorod, peanut and broken peanut structure found through ICP-OES (green) and EDS (blue) where x_{Ag} is [Ag]/([Ag]+[Au]).

(3) High Resolution Transmission Electron Microscopy (HRTEM)

(I) Nanorod

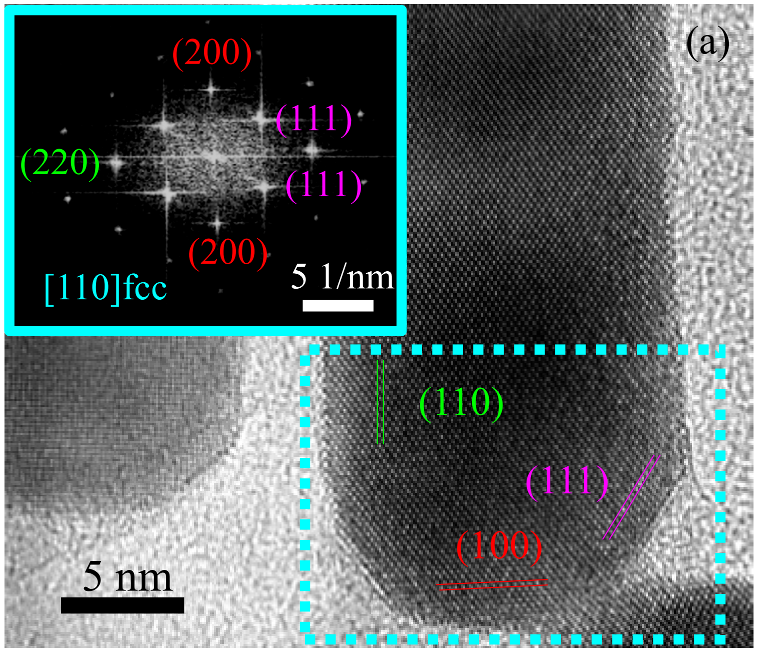

Figure S3-I: (a) High Resolution Transmission Electron Microscope (HRTEM) image and the corresponding Fast Fourier transform (FFT) image (inset) indicating the presence of {110}, {111} and {100} facets along [110] fcc zone axis of selected cyan region.

(II) Peanut (BP 0)

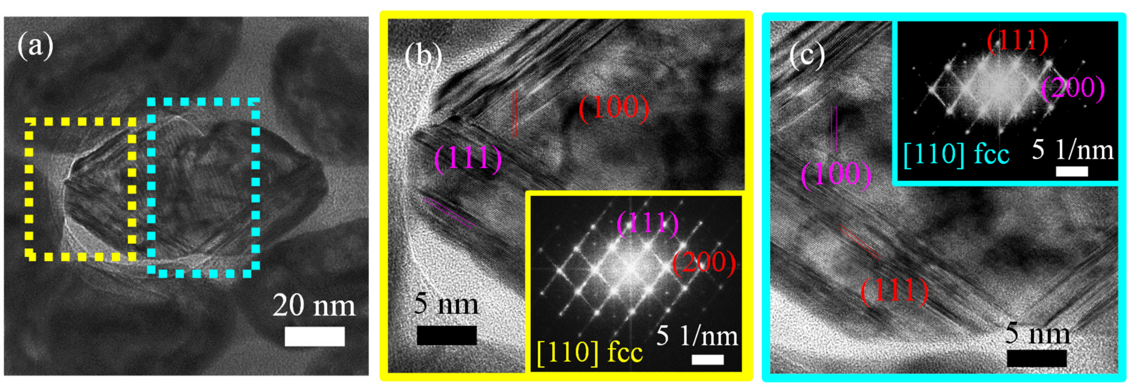

Figure S3-II:(a) TEM image of the peanut structure (BP0). The HRTEM image and corresponding FFT spot pattern (inset) of the selected region showing the presence of {100} and {111} along [110] zone axis at both corner (yellow box) (b) and the middle section of the particle (cyan box) (c).

(III) Broken Peanut (BP30)

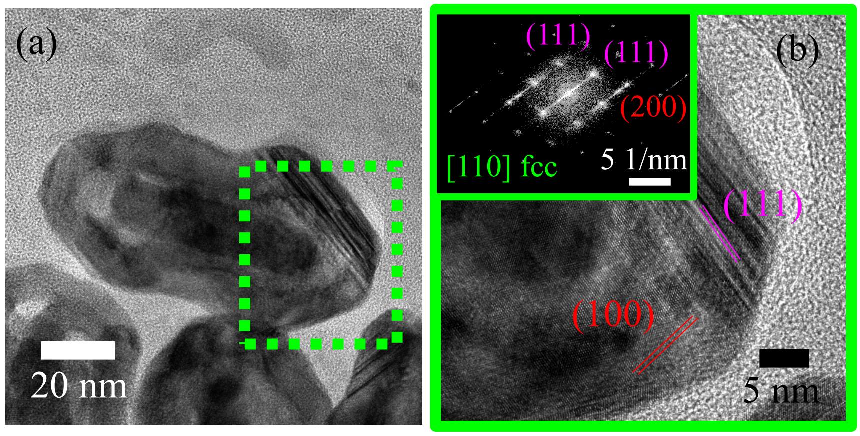

Figure S3-III: (a) TEM image of the broken peanut structure obtained at 30 minutes (BP30). (b) HRTEM image and the corresponding FFT spot pattern (inset) of the selected green region showing the presence of {100}and {111} facets along [110] zone axis.

(IV) Broken Peanut (BP60)

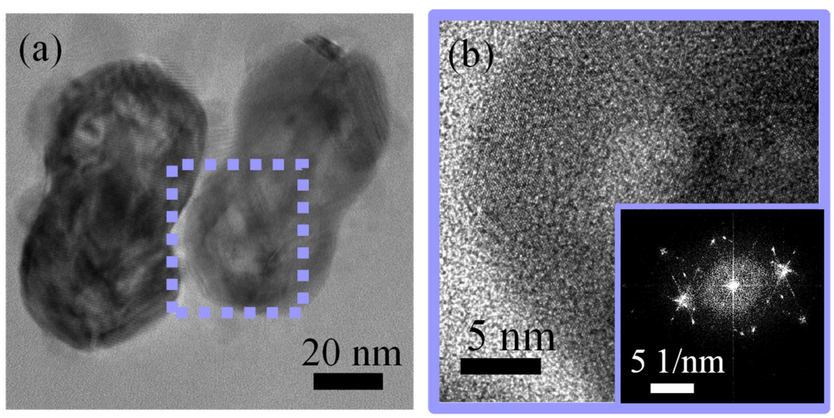

Figure S3-IV: (a) TEM image of the broken peanut structure obtained at 60 minutes (BP60). (b) HRTEM image and the corresponding FFT spot pattern (inset) of the selected purple region.

(4) Elemental Composition of formation of broken peanut with time through ICP-OES

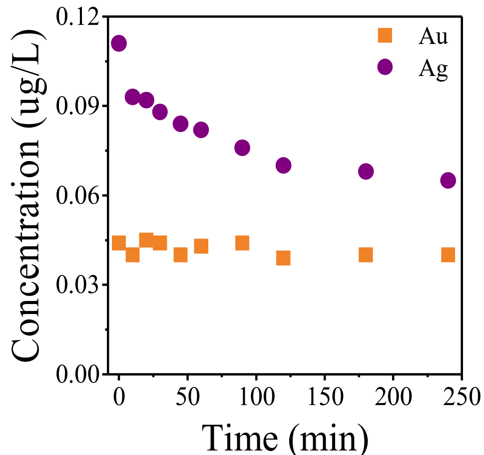

Figure S4: The evolution of broken peanut structure through dealloying of only Ag atoms from the peanut structure determined by taking ICP-OES at different time intervals. The concentration of Au remained same throughout the process which indicates the diffusion of only Ag atoms outside the structure during dealloying.

(5) Effect of different concentration of HCl

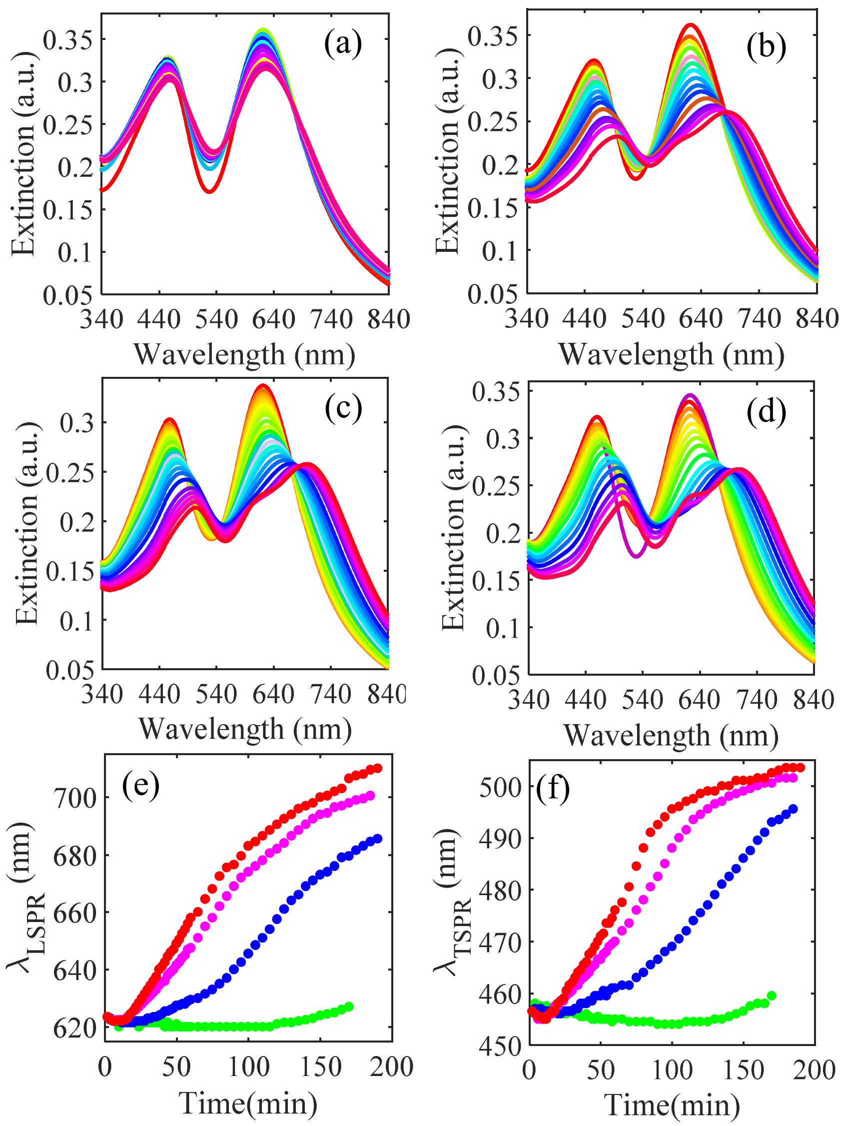

Figure S5: Evolution of extinction spectra with time at different HCl concentration of (a) 0.11M (b) 0.22M (c) 0.33M and (d) 0.55M.(e-f) Change in LSPR and TSPR wavelength with time at different HCl concentration of 0.11M(green), 0.22M (blue), 0.33M (magenta) and 0.55M (red).

(6) Effect of NaCl and HBr.

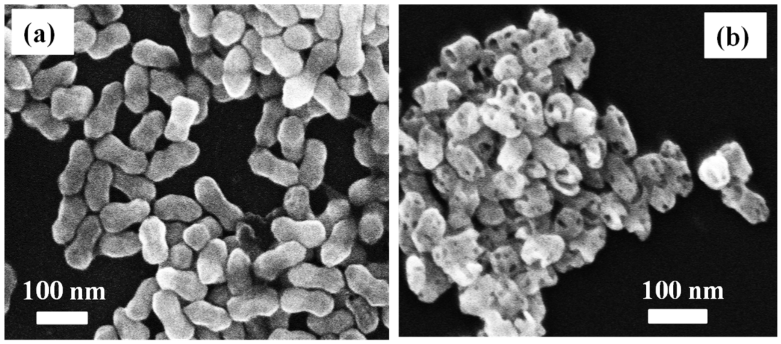

Figure S6: SEM image of peanut structure after treating it with 0.33 M of NaCl (a) and 0.33M of HBr (b).

(7) The formation of AgCl during the dealloying process

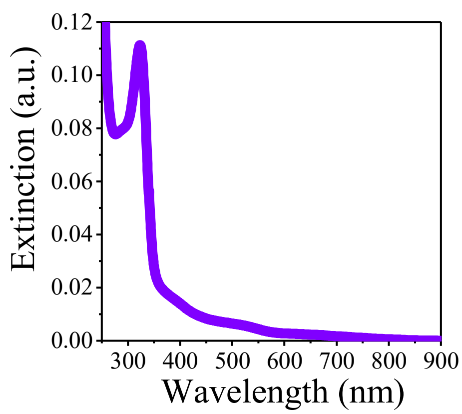

Figure S7: Extinction spectra of supernatant solution (purple) obtained after removing the broken peanut structure through centrifugation. The peak at 320 nm confirms the formation of AgCl.

(8) Reduction of 4 nitrophenol to 4 aminophenol

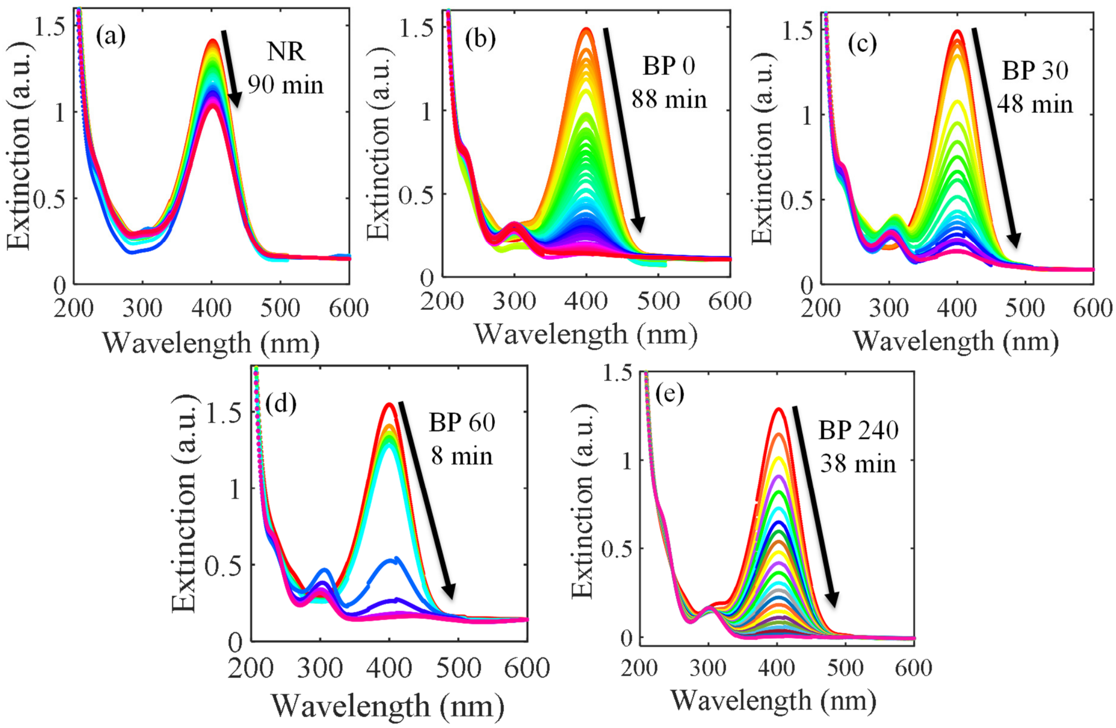

Figure S8: Extinction spectra of conversion of 4 nitrophenol to 4 aminophenol monitored through the decrease in the intensity at 400nm in presence of sodium borohydride with (a) NR (b) BP 0 (c) BP 30 (d) BP 60 and (e) BP240. In case of nanorod, reaction is very slow with only 25% reduction in intensity in 90 minutes.

(9) <u>Stability of the Nanoparticle after catalytic reaction</u>

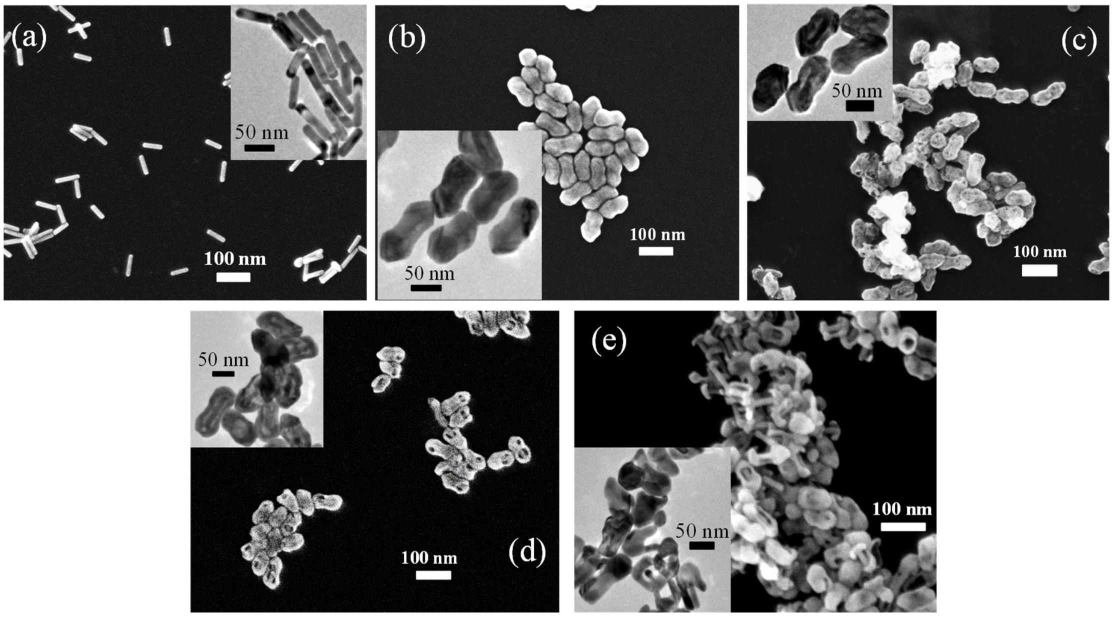

Figure S9: The SEM image and TEM image (in inset) of the nanostructure after catalysis reaction (a) Nanorod (b) BP0 (c) BP30 (d) BP60 (e) BP240. No change in the structure was observed after the reaction.

Table S1: The concentration of Ag and Au calculated using different techniques

Sample	**ICP-OES**		**EDS**		**XPS**	
	$\left(\frac{x_{Ag}}{x_{Ag}+x_{Au}}100\right)$ (x_{Ag})	$\left(\frac{x_{Au}}{x_{Ag}+x_{Au}}100\right)$ (x_{Au})	Ag (atomic %)	Au (atomic %)	Ag (atomic %)	Au (atomic %)
Nanorod	3.1% (*0.003 μg/L*)	96.9% (*0.093 μg/L*)	4%	96%	11%	89%
Peanut	76.6% (*0.111 μg/L*)	23.4% (*0.034 μg/L*)	75%	25%	60.7%	39.3%
Broken Shell Peanut	45.9% (*0.034 μg/L*)	54.1% (*0.040 μg/L*)	45%	55%	48.8	51.2

Table S2: The comparison of rate constant value obtained for solid and hollow nanostructures.

	Nanostructure	**Rate Constant**	**Ref**
Thota et al.	Solid nanorod Hollow nanorod	0.0169 s^{-1} 0.0257 s^{-1}	12
Zeng et al.	Solid nanocubes Nanocages	0.20 s^{-1} 2.83 s^{-1}	27
This work	Nanorod (NR) Peanut (BP0) Broken Peanut 30 (BP 30) Broken Peanut 60 (BP 60) Broken Peanut 240 (BP 240)	0.00362 min^{-1} (6.03 x 10^{-5} s^{-1}) 0.0326 min^{-1} (5.43 x 10^{-4} s^{-1}) 0.05340 min^{-1} (8.9 x 10^{-4} s^{-1}) 0.38812 min^{-1} (64.7 x 10^{-4} s^{-1}) 0.0769 min^{-1} (12.8 x 10^{-4} s^{-1})	-