Differential role of PVP on the synthesis of plasmonic gold nanostructures and their Catalytic and SERS properties

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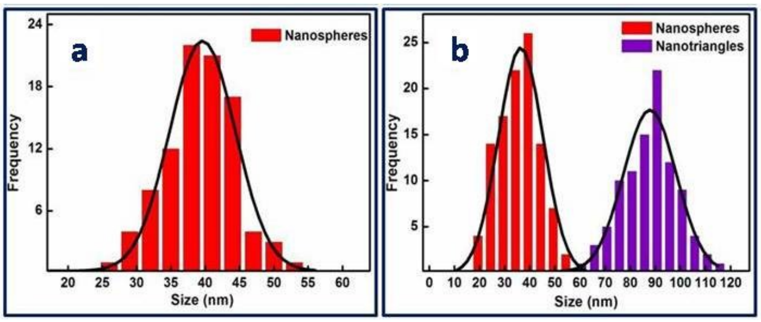


Fig. S1 Size distribution histogram of (a) nanospheres and (b) nanotriangles synthesized at room temperature.

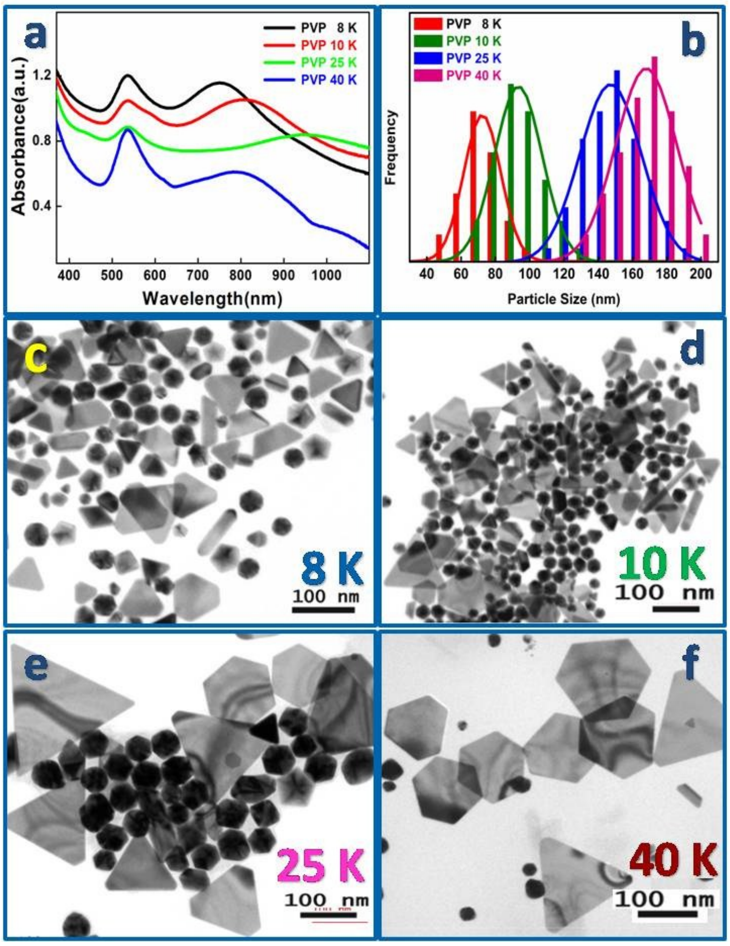


Fig. S2 (a) and (b) are absorption spectra and size distribution histogram of nanotriangles formed with different molecular weights of PVP. (c-f) are TEM images of nanotriangles formed by using PVP of molecular weight 8k, 10k, 25k and 40k respectively.

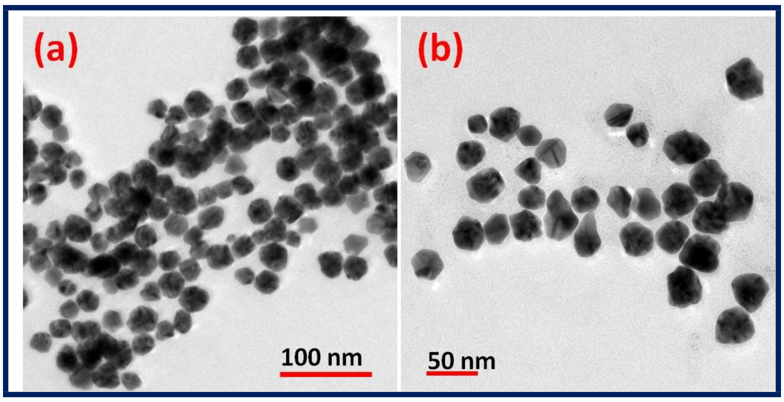


Fig. S3 TEM images of nanostructures formed with (a) NaCl and (b) NaI.

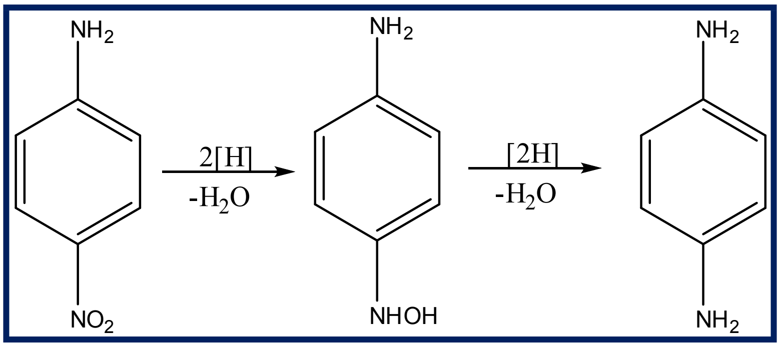
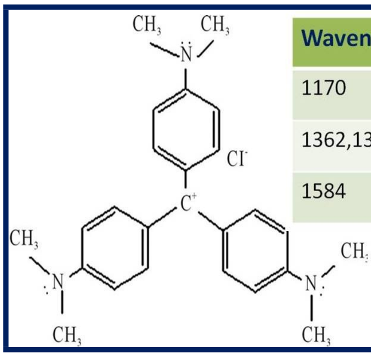


Fig. S4 Reduction mechanism of 4-nitroanniline to p- para–phenylenediamine by $NaBH_4$ in the presence of gold nanoparticles.



Wavenumber (cm^{-1})	Band Assignment
1170	Ring C-H bending
1362,1387	N-phenyl stretching
1584	Ring C-C stretching

Fig. S5 Structure of crystal violet and Raman band assignment corresponding to different modes of crystal violet.

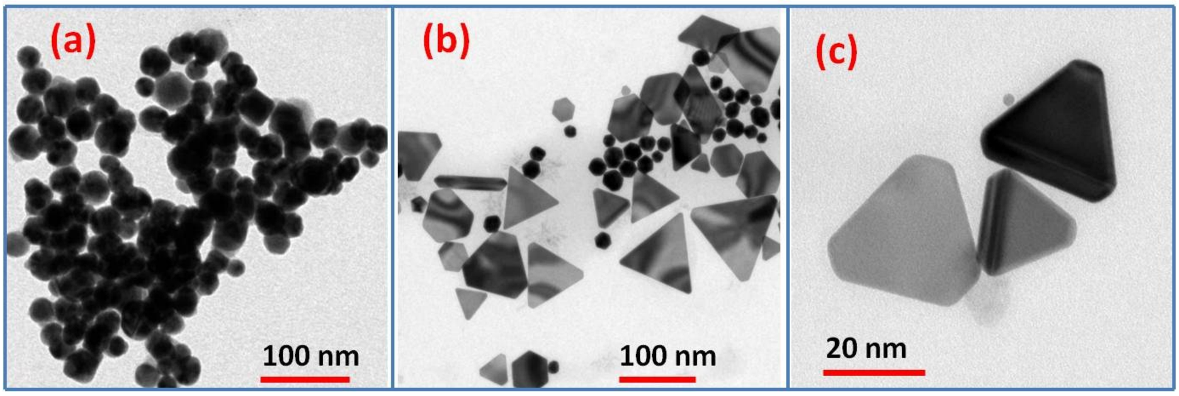


Fig. S6 The images of (a) spherical (b) large nanotriangles (c) small nanotriangles of Au represents the coupling with crystal violet molecules for SERS studies.

Table 1: d values of different crystallographic axes and average crystallite size for different nanoparticles as calculated by the Scherrer formula.

Au nanoparticles	d- values of different (*hkl*) planes			Average Crystallite size
	(*111*)	(*200*)	(*220*)	
Spherical particles	2.353	2.041	1.442	30.5 nm
Large nanotriangles	2.353	2.039	1.439	53.4 nm
Small nanotriangles	2.352	2.036	1.437	21.3 nm

Table 2 Intensity ratios of different crystallographic planes and their strain for different nanoparticles

Ratio of intensity	(*200*)/(*111*)	(*220*)/(*111*)	Strain along different (*hkl*) planes		
			(*111*)	(*200*)	(*220*)
Spherical particles	0.250	0.128	3.40 %	3.68 %	2.98 %
Large nanotriangles	0.237	0.111	3.29 %	3.52 %	2.55 %
Small nanotriangles	0.207	0.083	3.25 %	3.08 %	1.96 %

Calculation of SERS Enhancement factor for Crystal Violet adsorbed on different Shape/Sized gold nanostructures synthesized:

Average EF of the new substrate that can be defined as

$$EF = (I_{SERS}/N_{Surf})/(I_{RS}/N_{Vol}),$$

where $N_{Vol} = C_{RS} * V$ is the average number of molecules in the scattering volume (V) at concentration C_{RS} for the Raman (non-SERS) measurement, and N_{Surf} is the average number of adsorbed molecules in the scattering volume for the SERS experiments and I_{SERS} and I_{RS} denote the integrated intensities for the strongest band of the new surface and solution species. This definition is normally taken as representative of a substrate assuming a monolayer coverage.

To calculate EF, it is necessary to know the number of molecules in the focal area of the microscope for raman and SERS measurement. The drop volume of analyte taken was 10 uL that covers a surface area of about 10 mm^2 and spot area of the laser was calculated from the diameter of the laser spot of 20 um.

Area of laser spot $A = \pi \times r^2 = 3.14 \times (10\ um)^2 = 314\ um^2$

We can calculate the number of molecules for raman and SERS measurements in the drop considering ,

N = Volume x Conc. x NA

$N_{SERS} = (10 \times 10^{-6}\ L) \times (1 \times 10^{-6}\ M) \times (6.022 \times 10^{23}) = 6 \times 10^{12}$ molecules in the drop of SERS substrate. $N_{RAMAN} = (10 \times 10^{-6}\ L) \times (1 \times 10^{-3}\ M) \times (6.022 \times 10^{23}) = 6 \times 10^{15}$ molecules in the drop of SERS substrate. These molecules are in the drop area but we have to consider the number of molecules in the laser spot so by proportionality we obtain N_{Vol}= 1,13 X 10^{12} and N_{Surf}= 1,13 X 10^9 respectively. Putting the intensities of the peak at 1170 cm^{-1} (I_{SERS} = 23500 for small nanotriangles, 12661 for large nanotriangles and 4660 for spherical nanoparticles and I_{RS}= 250 and the number of molecules irradiated in normal Raman and SERS spectra to the formula EF = $(I_{SERS}/N_{Surf})/(I_{RS}/N_{Vol})$ we can obtained SERS enhancement factor for different nanostructures.