Supporting Information

Nanosilver Rainbow: A rapid and facile method to tune different colors of nanosilver through the controlled synthesis of stable spherical silver nanoparticles.

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The Investigation of Factors Affecting the Formation of AgNps

In this work the effect of reaction pH, reaction temperature, concentrations of $AgNO_3$, $NaBH_4$, tri sodium citrate and hydrazine sulphate on the synthesis of green colored silver nanoparticles (GAgNps) were investigated.

Effect of Silver Nitrate Concentration

The concentration of silver nitrate was varied as given in the experimental section of the manuscript while keeping the other factors constant. Figure S.1 displays the corresponding UV/Vis spectra while Table S.1 summarizes the data. According to Figure S.1 the absorbance of the peak around 400 nm increases with increase in $AgNO_3$ concentration. This observation is in good agreement with previous reports.

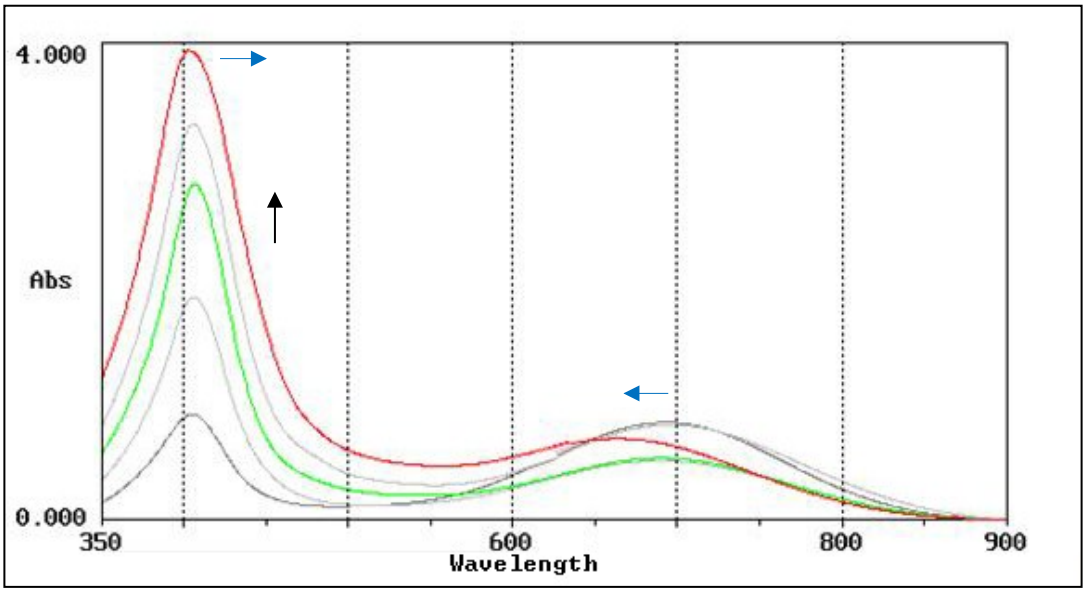


Figure S.1 - Effect of concentration of $AgNO_3$ on the formation of GAgNps

Table S.1 - Extinction and the Corresponding Wavelength of the Extinction Maxima of GAgNps with different concentrations of silver nitrate

$[AgNO_3]$ (mol dm^{-3})	Peak 1		Peak 2	
	Wavelength (nm)	Extinction	Wavelength (nm)	Extinction
1×10^{-3}	405.0	0.890	700.5	0.819
2×10^{-3}	406.5	1.872	699.0	0.495
3×10^{-3}	406.0	2.817	697.0	0.519
4×10^{-3}	407.0	3.322	696.0	0.798
5×10^{-3}	407.5	3.949	663.5	0.684

Effect of Sodium Borohydride Concentration

In order to check the effect of reducing agent, sodium borohydride concentration was varied, keeping the other factors constant. Figure S.2 displays the UV/Vis peak positions and the intensities while Table S.2 summarizes the data.

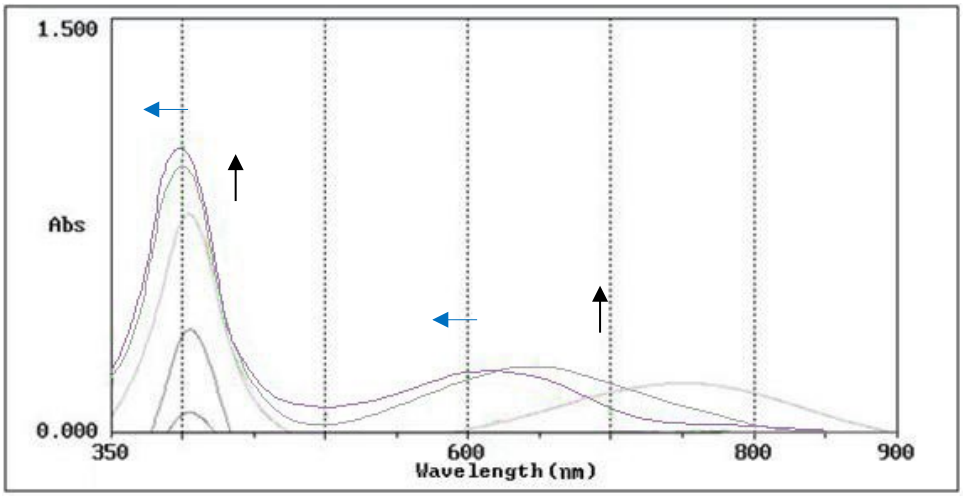


Figure S. 2- Effect of concentration of $NaBH_4$ on the formation of AgNps

Table S.2 - Absorbance and the Wavelength of the two peaks of GAgNps with different concentrations of sodium borohydride

Concentration of Sodium Borohydride (mol dm^{-3})	Peak 01		Peak 02	
	Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance
1×10^{-3}	405.0	0.075	-	-
2×10^{-3}	405.0	0.375	-	-
3×10^{-3}	404.5	0.794	755.0	0.181
4×10^{-3}	403.5	1.038	681.0	0.205
5×10^{-3}	402.5	1.042	613.0	0.210

Effect of Tri Sodium Citrate Concentration

In order to see the effect of tri sodium citrate, the concentration of tri sodium citrate was varied while the other factors were kept constant. Figure S.3 displays the UV/Vis peak positions and the intensities while Table S.3 summarized the data.

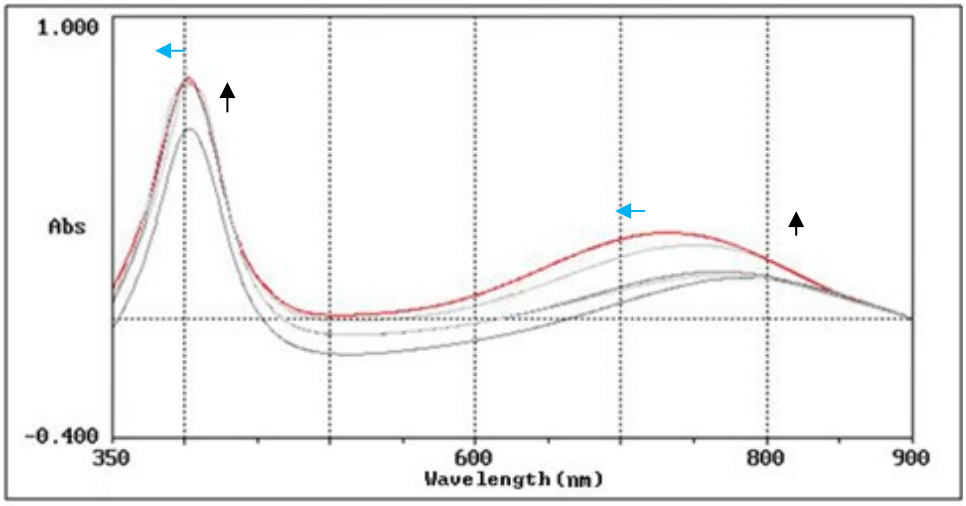


Figure S.3 - Effect of concentration of tri sodium citrate on the formation of GAgNps

Table S.3 - Absorbance and the Wavelength of the two peaks of AgNps with different concentrations of tri sodium citrate concentration

Concentration of Tri sodium Citrate (mol dm^{-3})	Peak 01		Peak 02	
	Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance
0.010	404.5	0.625	786.0	0.144
0.020	403.5	0.752	777.5	0.154
0.030	403.0	0.772	770.0	0.156
0.040	402.5	0.786	777.5	0.243
0.050	402.0	0.886	730.0	0.283

Effect of Hydrazine Sulphate Concentration

Effect of hydrazine sulphate was monitored by varying the concentration of hydrazine sulphate, while keeping the other factors constant. Table S.4 summarized the data. Table S.4 shows the pH variations of the reaction mixture and neat hydrazine sulphate solutions. UV/Vis spectra are shown in Figure S.4. According to Table S.5, the pH of the three solution mixtures are different. At pH 9.30, only yellow color was observed. These results are also in agreement with these published data for yellow color. However, no reports are there where they claim the pH effect on formation of spherical shape AgNps other than yellow color AgNps.

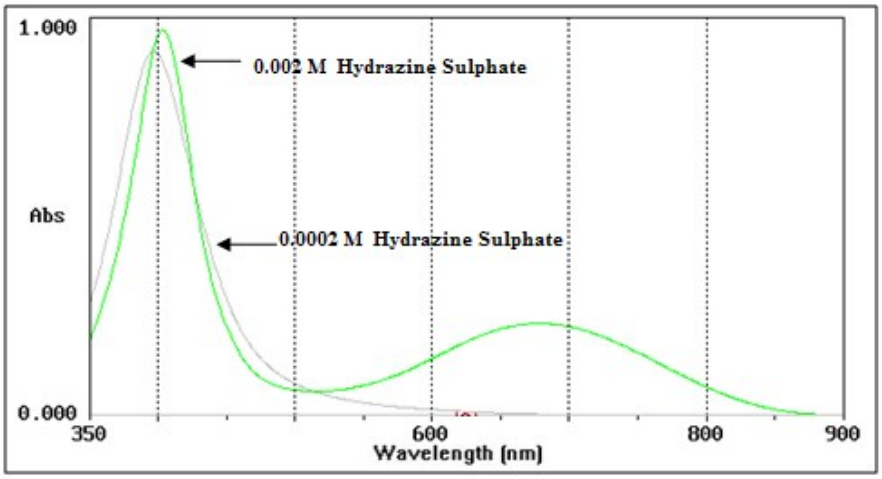


Figure S.4 - Effect of concentration of hydrazine sulfate on the formation of GAgNp

Since neat hydrazine sulphate solutions are acidic in nature as shown in Table S.5, we have selected 2×10^{-3} M as the optimum concentration of hydrazine sulphate. It gives a pH around 7 to the medium. It is very clear that hydrazine acts as a supportive reducing agent by giving a better environment with a pH variation to form distinctive colors of AgNps.

Table S.4 - Absorbance and the Wavelength of the two peaks of GAgNps with different concentrations of hydrazine sulfate

Concentration of Hydrazine Sulphate (mol dm^{-3})	Peak 01		Peak 02	
	Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance
2×10^{-4}	397.0	0.917	-	-
2×10^{-3}	403.5	0.971	678.0	0.231
0.020	-	-	-	-

Table S.5 - pH variations of reaction mixtures, and neat hydrazine sulphate solutions of different concentrations

Concentration of Hydrazine Sulphate (M)	pH of Hydrazine Sulphate solution (at 30.1 ^{o}C)	pH of the reaction mixer after adding Hydrazine Sulphate (at 30.1 ^{o}C)
2×10^{-4}	3.34	9.30

2×10^{-3}	2.14	7.58
0.020	1.46	2.50

Effect of Temperature

In this experiment the temperature of the reaction medium was maintained at room temperature, 50 ^{o}C, 70 ^{o}C and 100 ^{o}C while the other factors were kept constant. Figure S.5 displays the UV/Vis peak positions and the intensities while Table S.6 shows the data obtained.

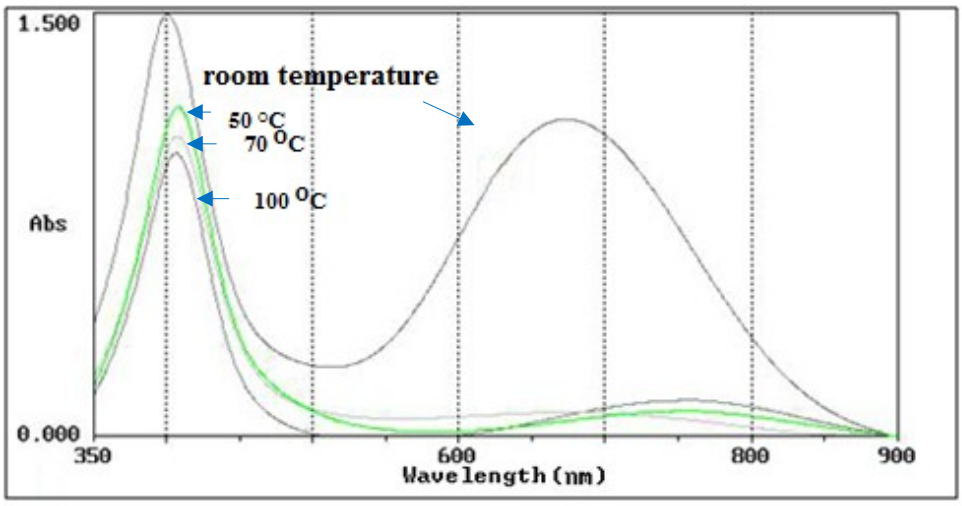


Figure S.5- Effect of reaction temperature on production of AgNps

The red shift observed and the broadening of the absorbance peak with increase in temperature are in accordance with formation of large particles. It is recorded that the increasing of the reaction temperature aids the growth of the crystal around the nucleus which leads to decrease in absorption.

Table S.6 - Absorbance and the Wavelength of the two peaks of GAgNps while varying the temperature of the system

Temperature (^{o}C)	Peak 01		Peak 02	
	Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance

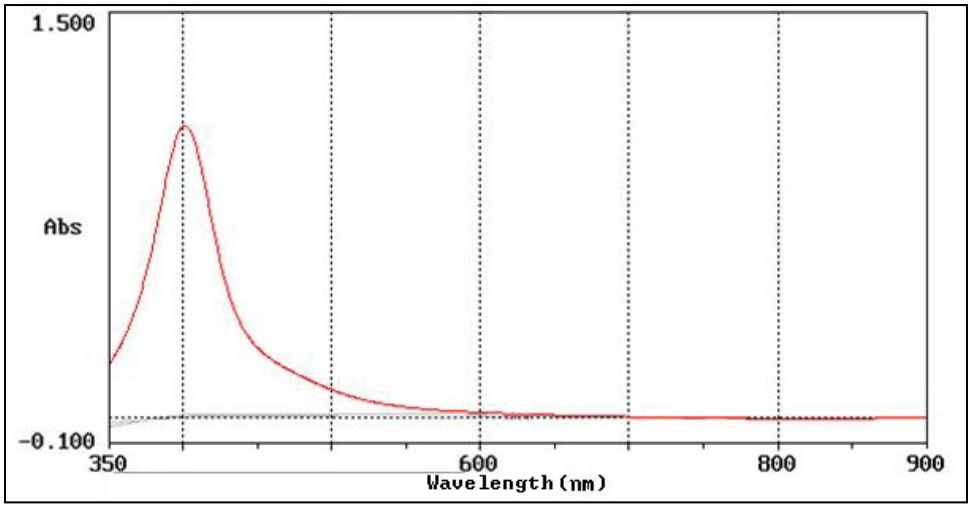
Room temperature	400.5	1.497	673.5	1.125
50	406.5	1.164	756.5	0.129
70	407.5	1.064	766.0	0.090
100	408.0	1.005	770.5	0.085

Effect of pH

For this investigation the pH effect was observed in there different ways as described in the experimental section. The synthesis of GAgNps was carried out in three different buffer solutions around pH 4, 7, 10. In the experiment all the other factors were kept constant.

Again this proves that a pH above 9 is required to obtain yellow colored AgNps. As shown in the Figure S.6 there was only a one peak with the addition of the pH 10.98 buffer solutions. No reaction occurred with the addition of the pH 4.76 buffer. Hence there was no particle formation at pH 4.76. A gray color appeared at the end of the reaction in the pH 7.11 buffer indicating macro size particle formation. Acidic condition suppress the formation of AgNps but basic conditions enhance their formation. It is clear that, at higher pH (pH~10), however, a large number of functional groups available for silver binding facilitated a higher number of AgNps to bind and subsequently form a large number of nanoparticles with smaller diameters.

		Peak 01



		Wavelength (nm)	Absorbance
CH_3COOH/ CH_3COONa	4.76	-	-
Na_2HPO_4 / $NaH_2PO_4.2H_2O$	7.11	-	-
$NaHCO_3$ / $Na_2CO_3.3H_2O$	10.98	401.0	1.081

Figure S.6 - Effect of reaction pH on formation of GAgNps (Green procedure)

Table S.7 - Absorbance and the Wavelength of the two peaks of GAgNps while varying the pH of the reaction system

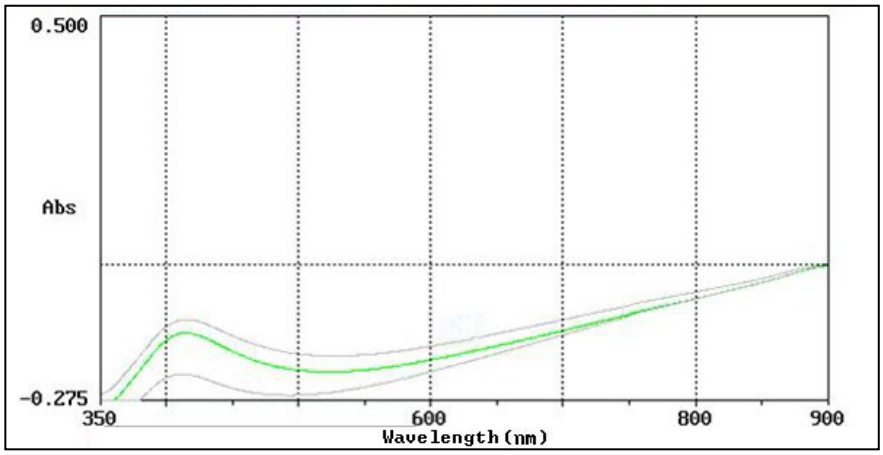


Figure S.7 - Effect of reaction pH on formation of silver nanoparticles (Green procedure) (without tri sodium citrate))

The next step was to identify whether the citrate ligands could be replaced by ligands such as acetate, phosphate and carbonate used to make the buffer solutions. Experiments show that the pH 7 and pH 10 medium can temporally make yellow colored AgNps but that they disappear as soon as the addition of $AgNO_3$ is over. A blackish gray color solution was formed with a gray color deposit. Furthermore the UV/Vis spectra (Figure S.7) of above solutions show only a small absorbance indicating, that no AgNps were stabilized in the medium. This implies that citrate cannot be replaced by the ligands of the buffer solutions as ligands of the buffer solutions cannot act as stabilizing agents. Furthermore, this experiment indicates that the reaction needs citrate ions as a stabilizing agent. The spectrum observed indicated that very few nanoparticles were formed.

The reducing power of the buffer solutions was tested. The experiments show no reaction in the medium suggesting that ligands of buffers could not alter the reaction unless giving a pH environment. The above results on the effect of pH suggest some interesting facts. pH has major effect on the formation of AgNps. According to the results it clearly depicts that the all colors have been produced between pH 7.28 – 8.39. Furthermore it can be stated that the method required the maintenance of the pH between 7.28 -8.39. A buffer could easily be used, if needed to maintain the pH of this reaction medium, without affecting the morphology of AgNps due to the fact that buffer ligands have no effect on formation of AgNps since the buffer cannot play a role as a reducing agent or a stabilizing agent.