

Summer 2019 – May to July

SYNTHESIS OF NANO-PARTICLES

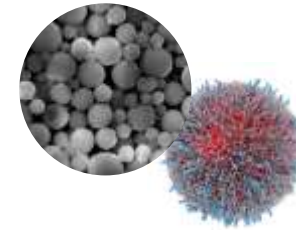
(Fed – Batch & Continuous Methods)

Summer Research Internship under the guidance of
Dr. S Venugopal, IISc Bengaluru

By
Koushik Sampath, NIT Trichy

Introduction

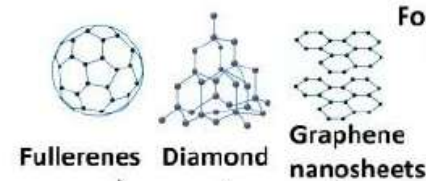
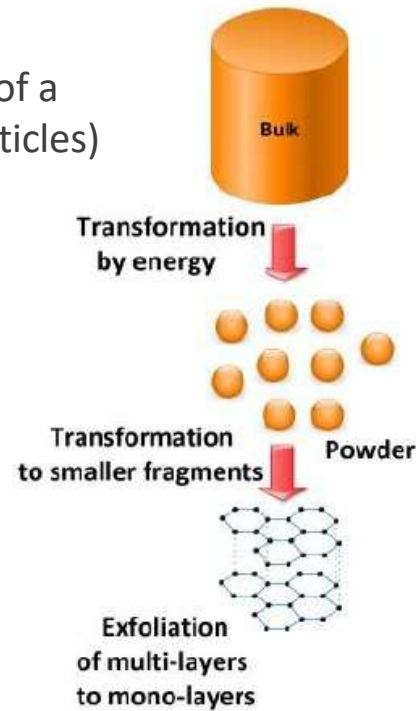
Nano particles are particles generally in the size range of 1nm to 100 nm. When bulk particles are normally reduced to that size, they have various property changes in terms of physical, chemical and optical properties owing to which they have a wide range of uses from drug delivery to energy applications.



There are 2 approaches of producing nano particles :

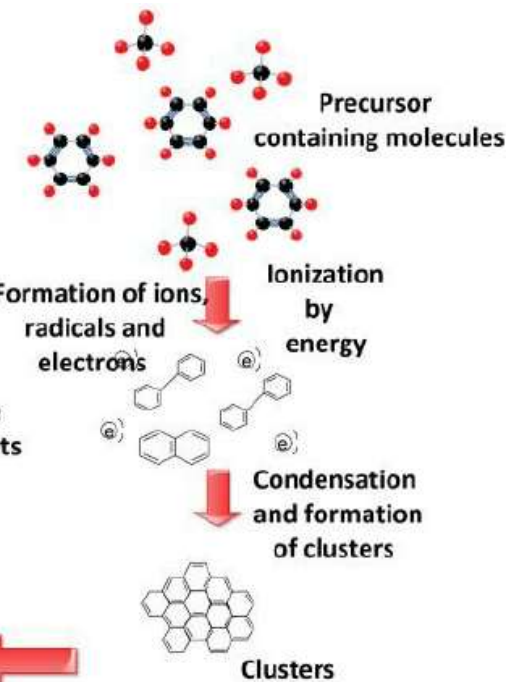
Top down approach

(slicing or successive cutting of a bulk material to get nano sized particles)

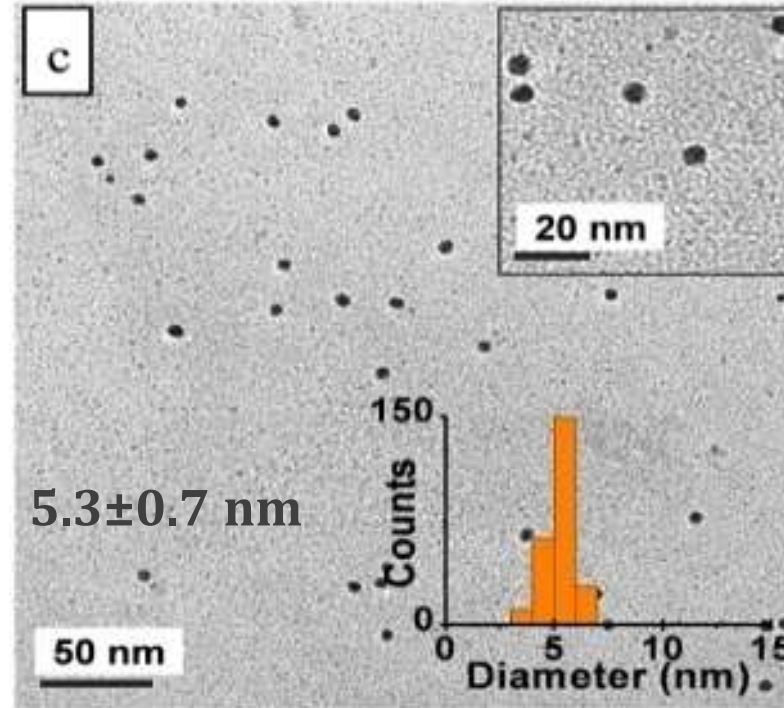
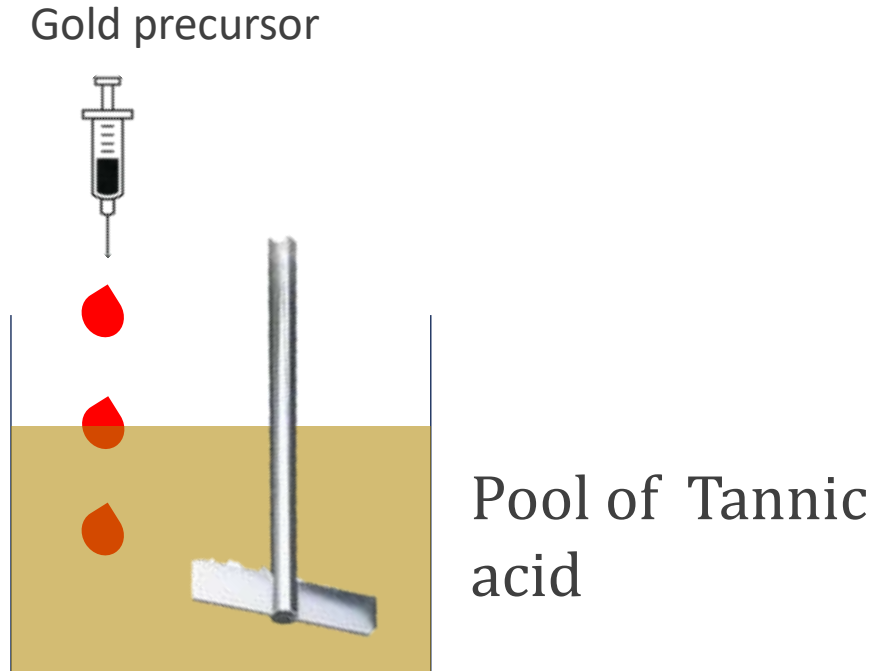


Bottom up approach

(create themselves by self assembly)



Sankar's Protocol



- Dropwise addition of Tannic Acid
- Formation of Seeds which act as growth sites



Experiments

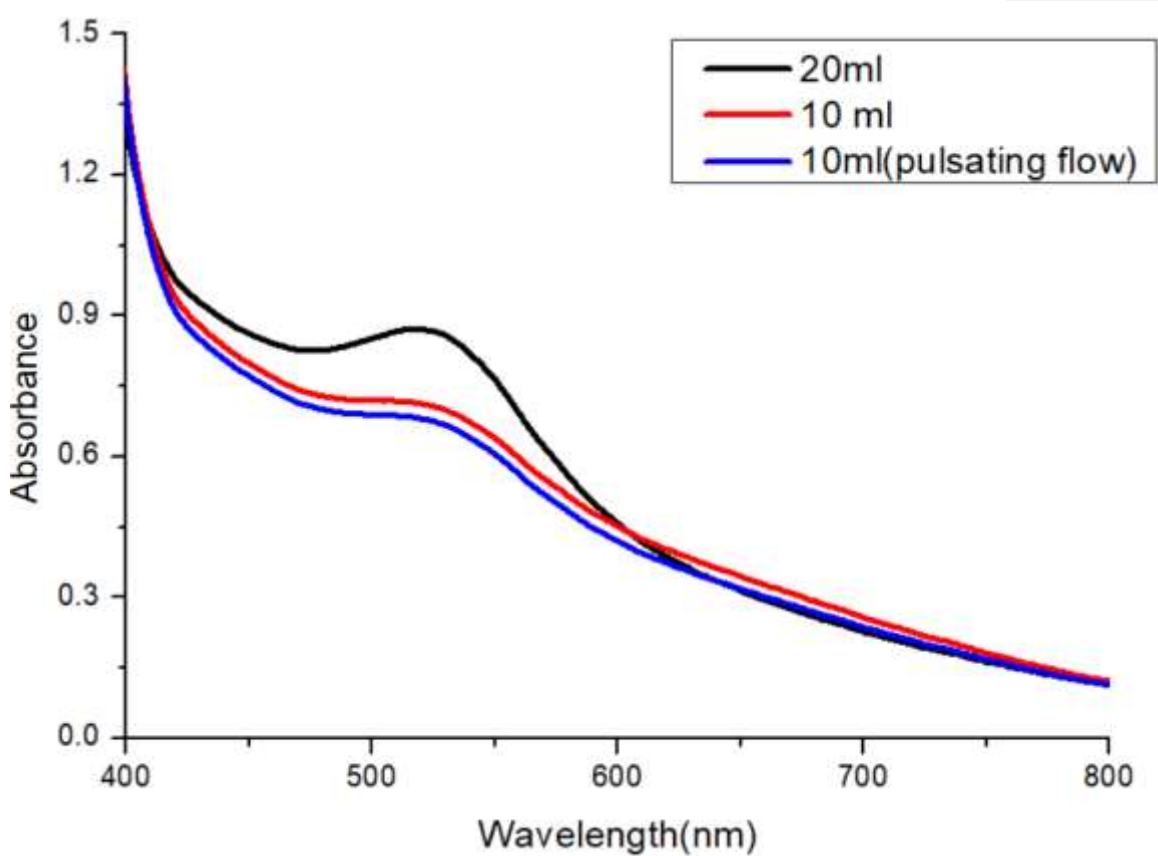
Set-up



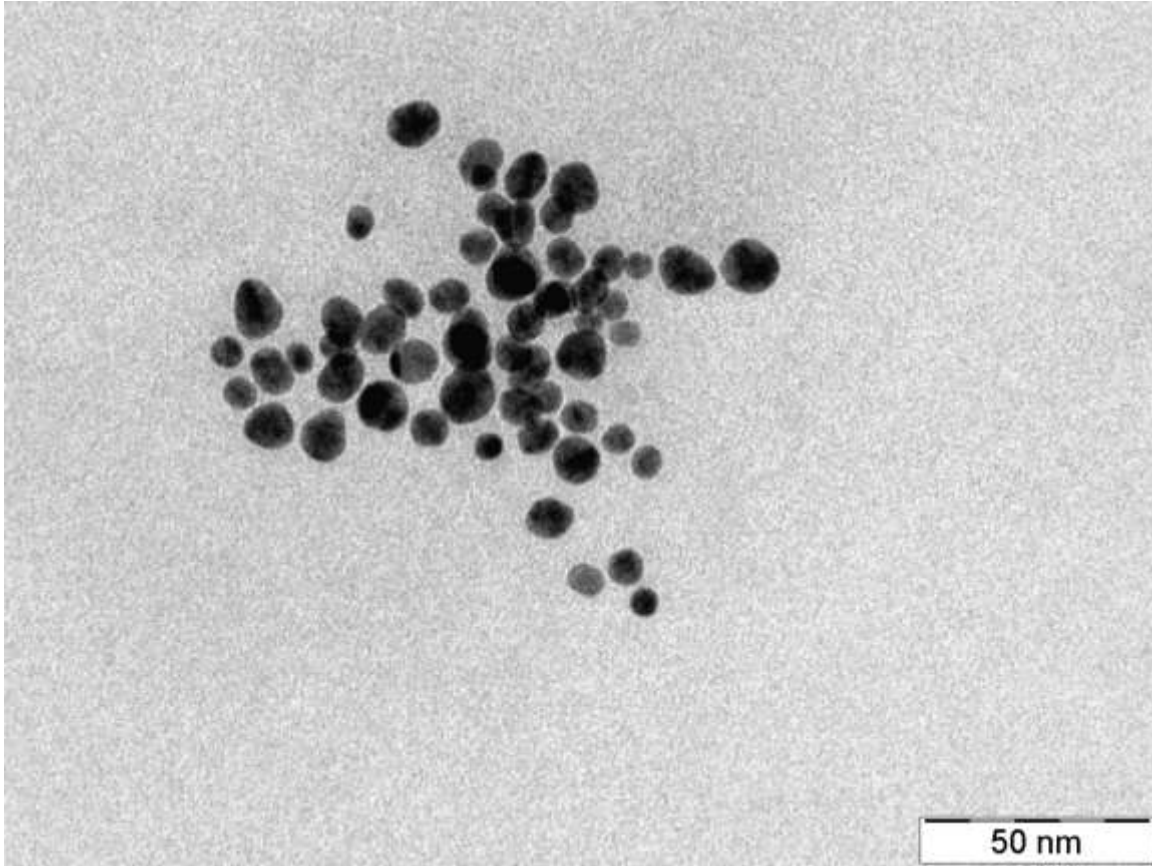
Experiment 1 : Fabrication of Gold Nano Particles

- **Tannic Acid solution** : 0.89mM. pH adjusted to 10 by using 1 w/v of Potassium Carbonate solution.
- **Chloroauric Acid solution** : 0.64 mM.
- Solutions are prepared with DI water.
- 15 ml of Tannic Acid solution is taken in 3 beakers, 10 and 20.5 ml of gold salt is added

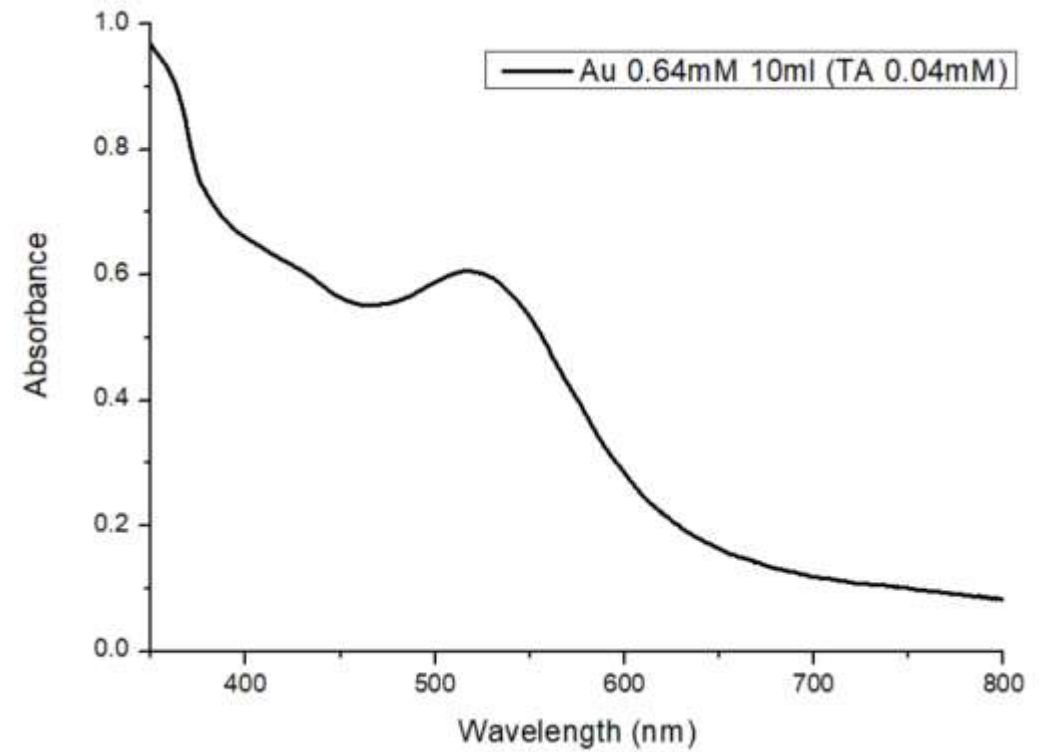
Impeller Rotation – 1000 rpm Chloroauric Acid : 0.64 mM Tannic Acid : 0.89 mM					
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25					
Sample	Input mode	V of Tannic Acid (ml)	V of Chloroauric Acid (ml)	pH of final solution	Amount of gold in the solution (mg)
1	Pulsating	15	10	8	1.2608
2	Dropwise	15	10	7 - 8	1.2608
3	Dropwise	15	20.5	7	2.5847



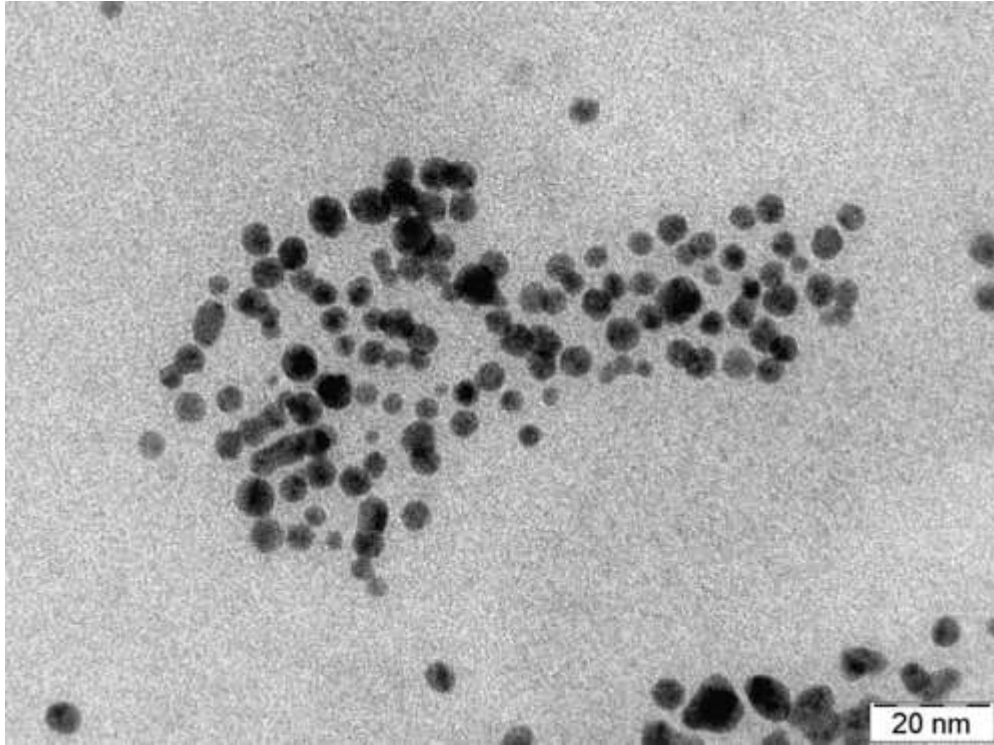
Gold Nanoparticles : TA 0.04mM



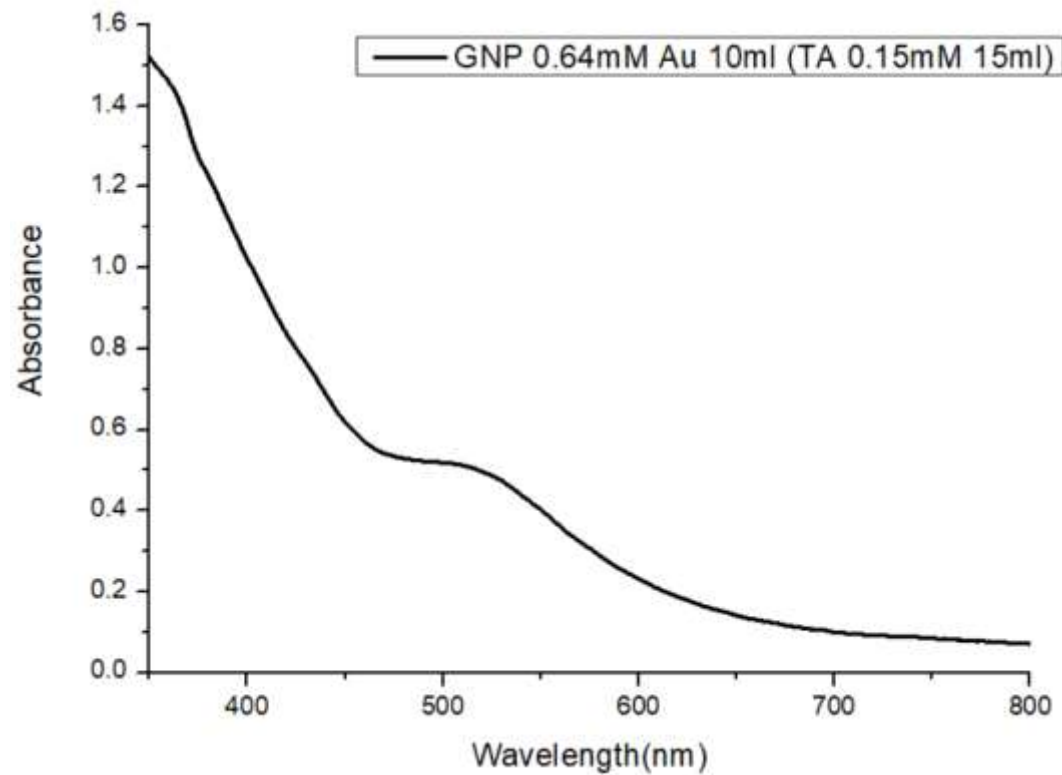
Avg. Size : 5.1 ± 1.9 nm



Gold Nanoparticles : TA 0.15mM



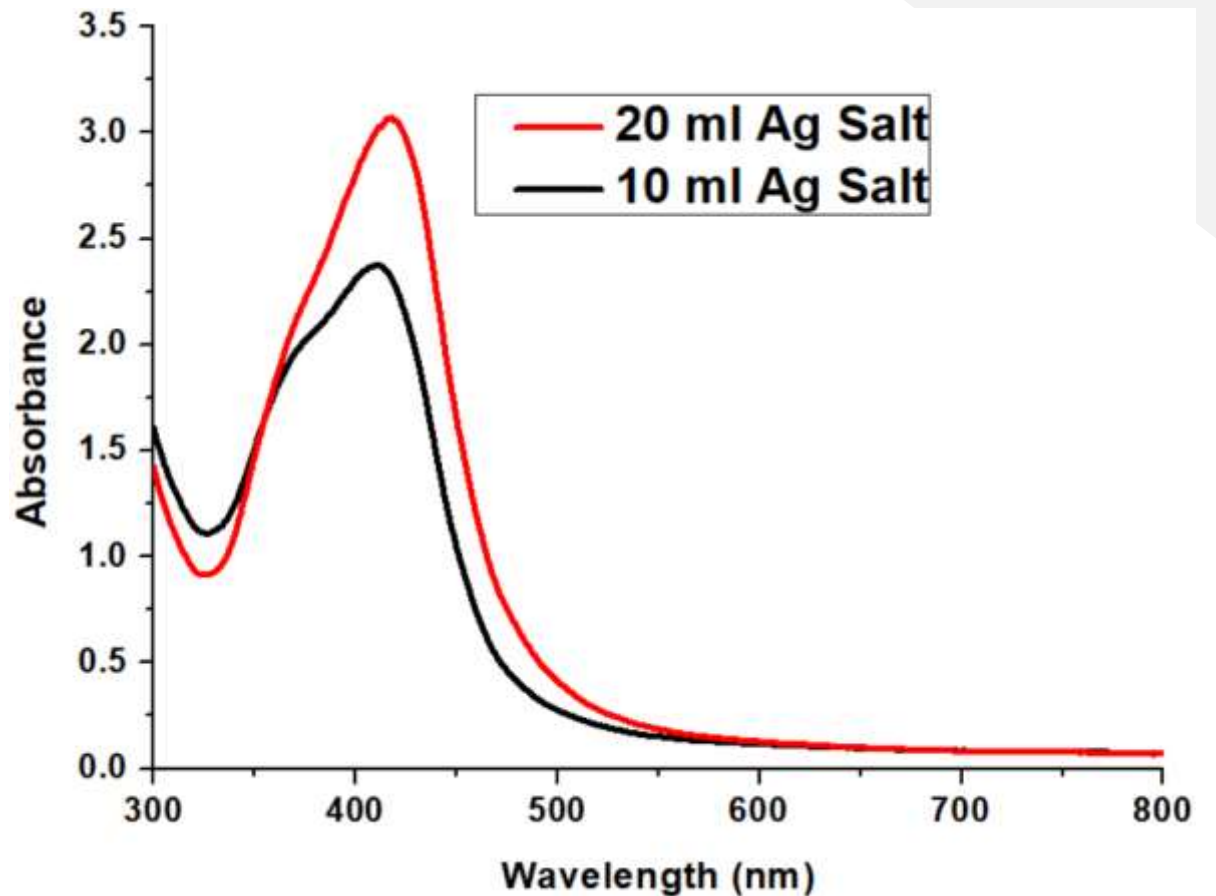
Avg. Size : 4.5 ± 0.9 nm



Experiment 2 : Fabrication of Silver Nano Particles

- **Tannic Acid solution** : 0.04mM. pH adjusted to 8.0 by using 1 w/v of Potassium Carbonate solution.
- **Silver Nitrate solution** : 0.64 mM.
- Solutions are prepared with DI water.
- 15 ml of Tannic Acid solution is taken in 2 beakers, 10 and 20 ml of silver salt is added

Impeller Rotation – 1000 rpm Silver Nitrate : 0.64 mM Tannic Acid : 0.04 mM				
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25				
Sample	Input mode	V of Tannic Acid (ml)	V of Silver Nitrate (ml)	pH of final solution
1	Dropwise	15	10	7
2	Dropwise	15	20	6 - 7



Core-Shell

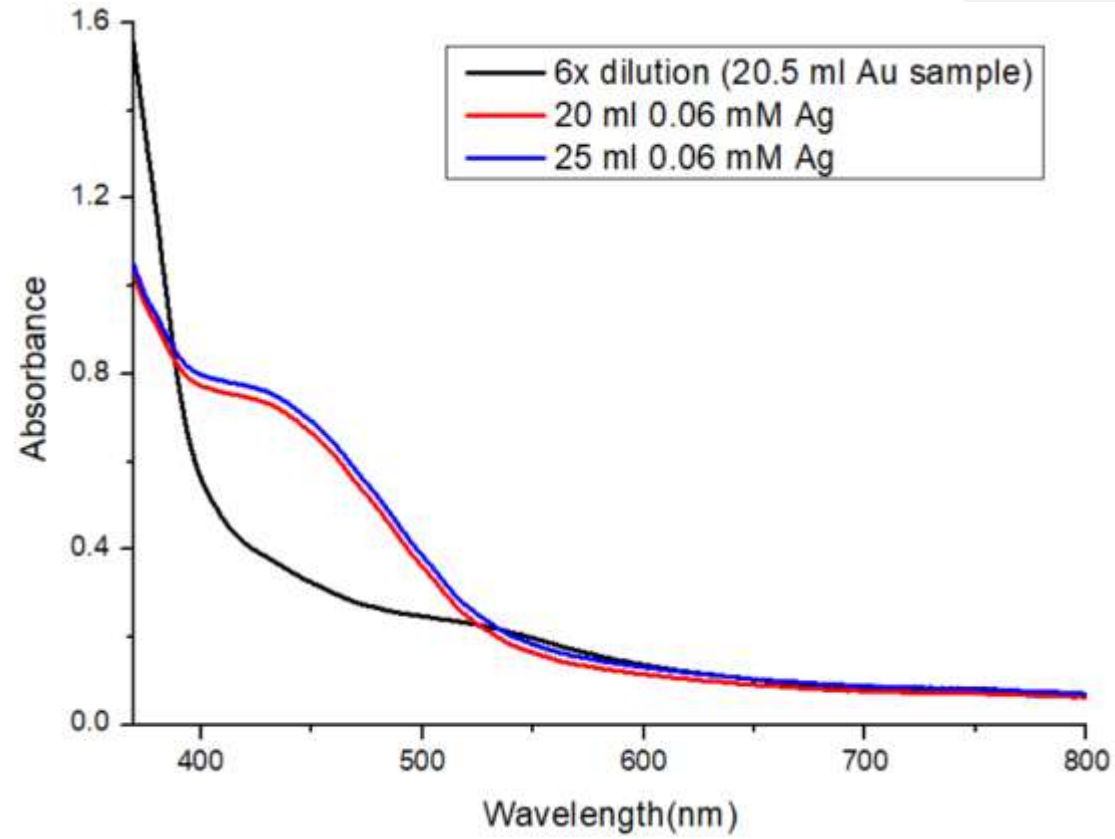
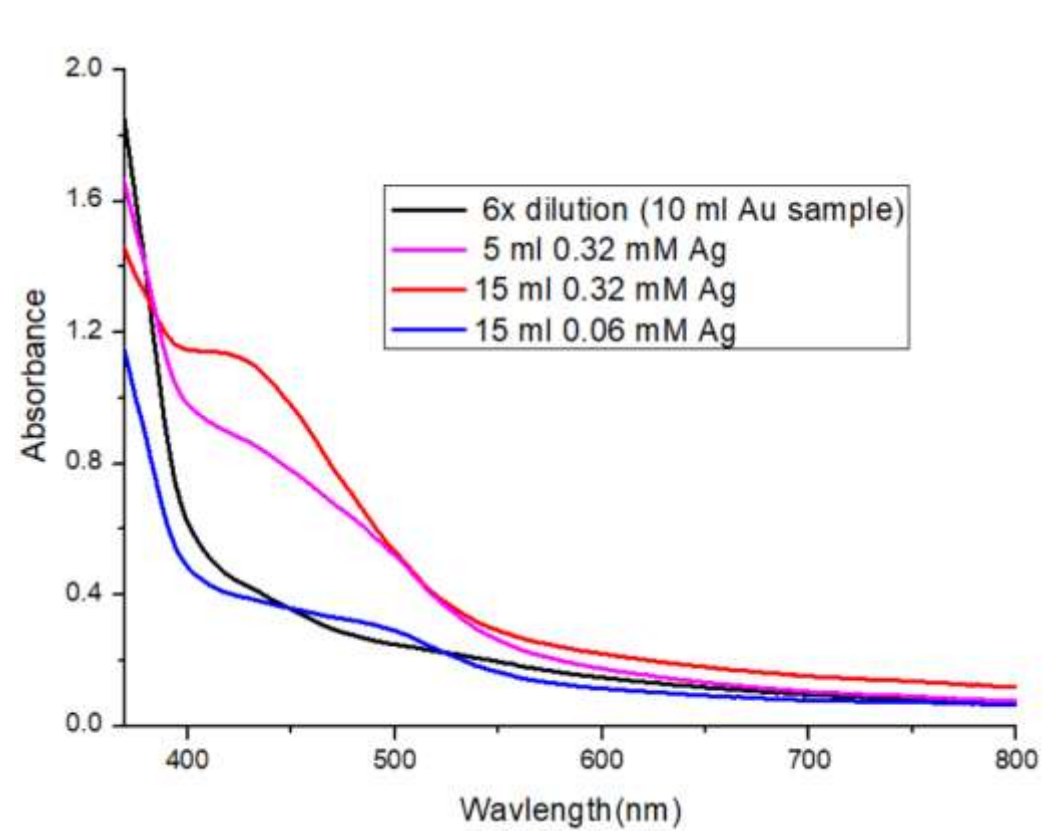
Au core – Ag shell

- Dilution
- Without dilution
- Centrifugation
- Combinations

Experiment 3 : Dilution (Au core Ag shell)

- **GNP Samples** : 2.5 ml made up to 15 ml (core solution)
- **Silver Nitrate solution** : 0.32 mM | 0.06 mM
- (shell solution)
- Solutions are prepared with DI water.
- 15 ml of GNP sample is taken in 5 beakers, silver salt solution is added

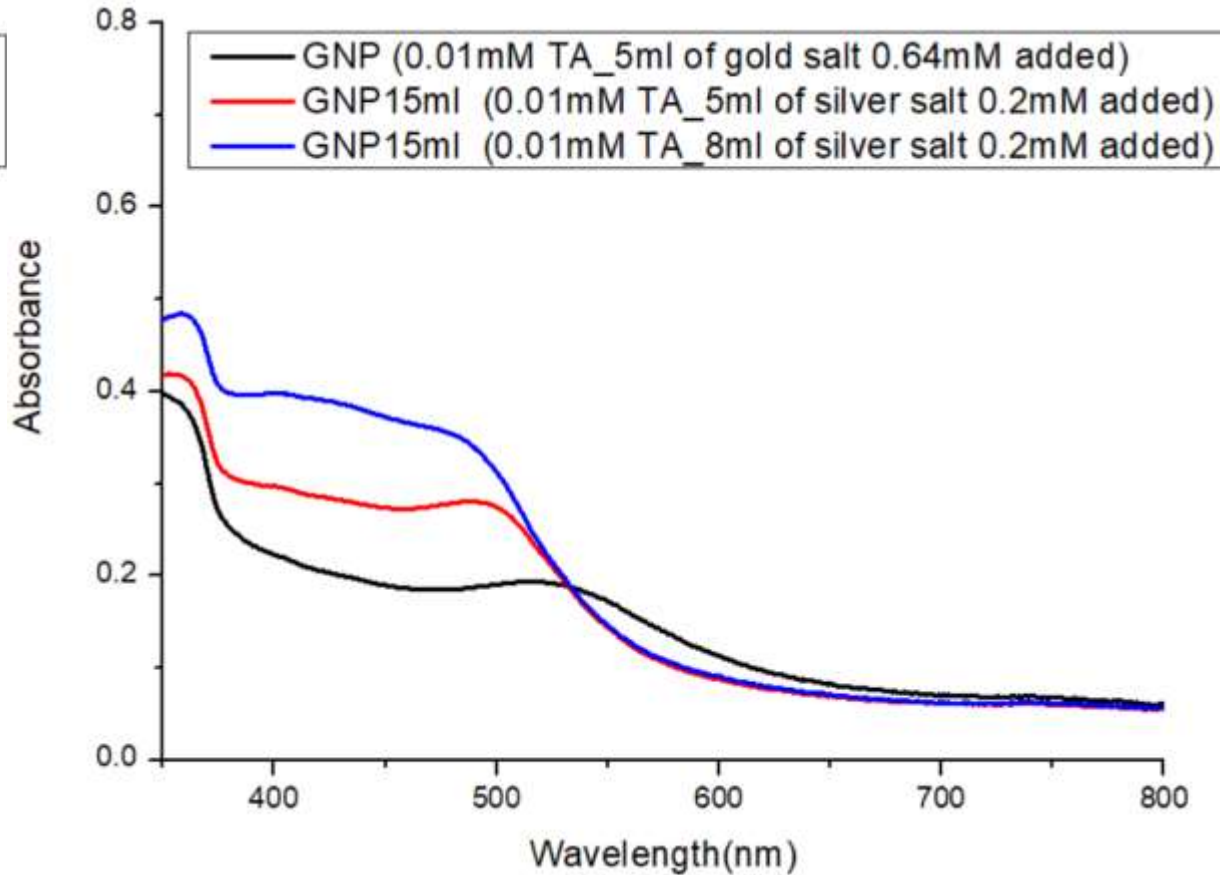
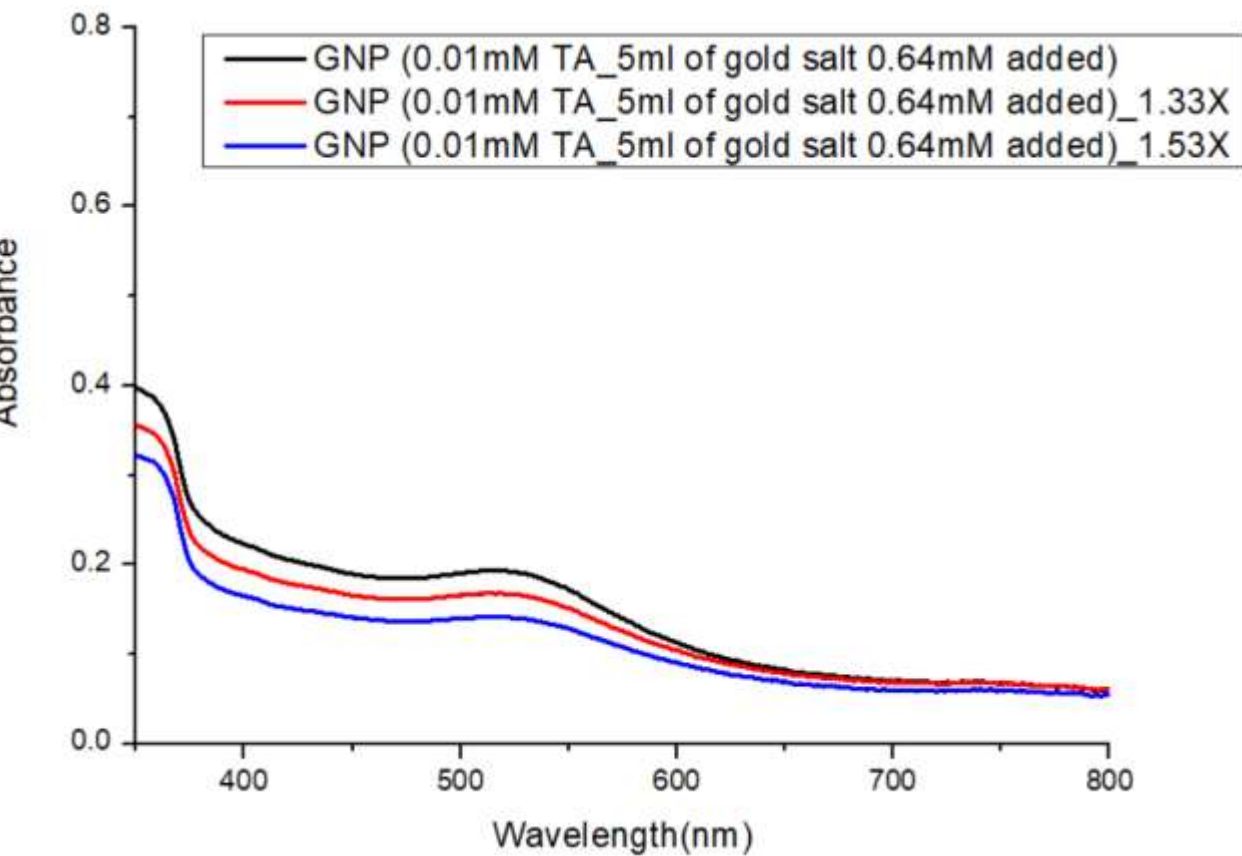
Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM & 0.32 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.32	5	7
2	Dropwise	10	15	0.32	15	6 – 7
3	Dropwise	10	15	0.06	15	7
4	Dropwise	20.5	15	0.06	20	7
5	Dropwise	20.5	15	0.06	25	6 – 7

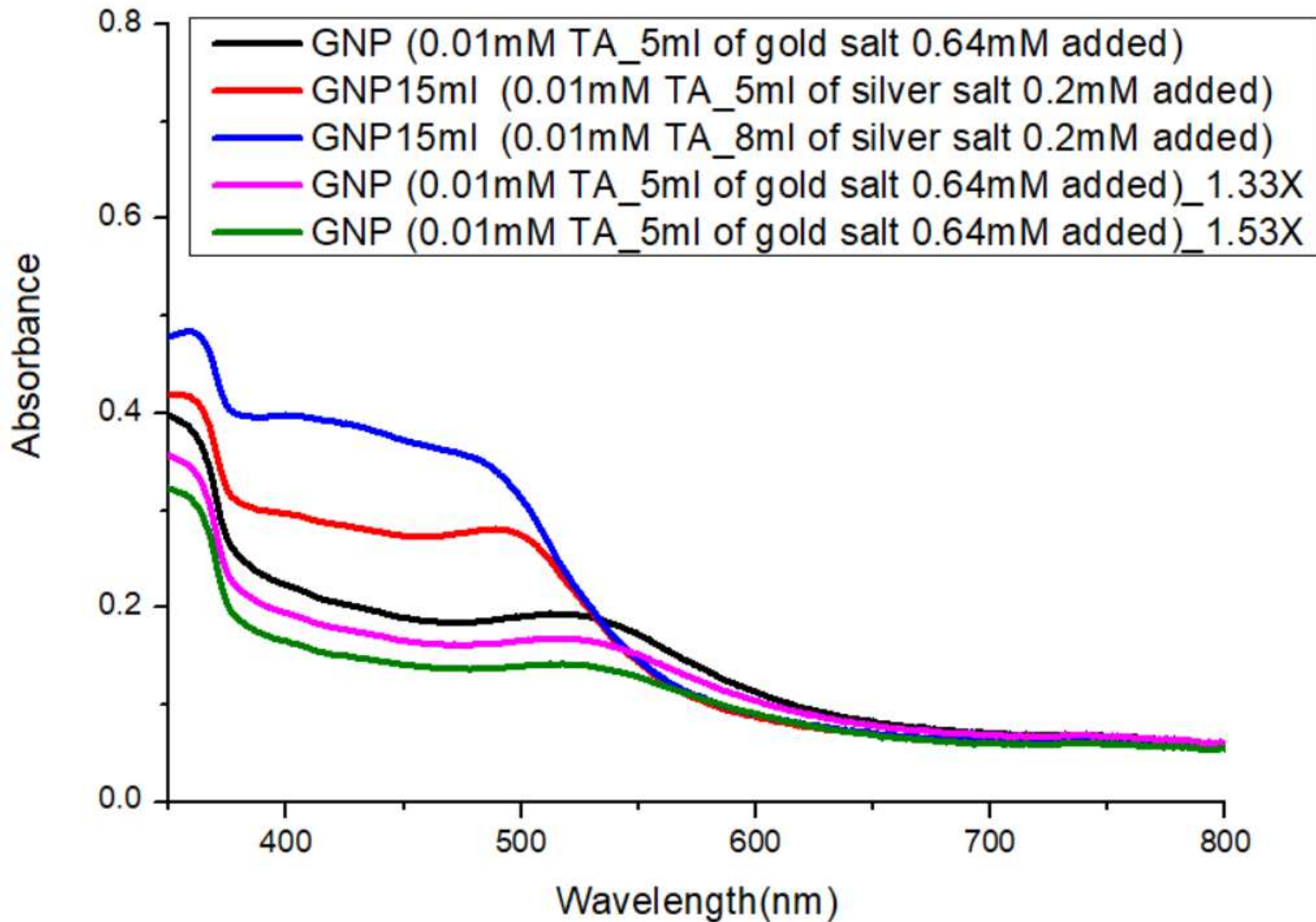


Experiment 4 : No dilution (Au core Ag shell)

- **GNP Samples** : 15 ml (core solution : no dilution) (TA 0.01mM)
- **Silver Nitrate solution** : 0.2 mM (shell solution)
- Solutions are prepared with DI water.
- 15 ml of GNP sample is taken in each beaker, silver salt solution is added

Impeller Rotation – 1000 rpm Silver Nitrate Solution : 0.2 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	5	15	0.2	5	8
2	Dropwise	5	15	0.2	8	8

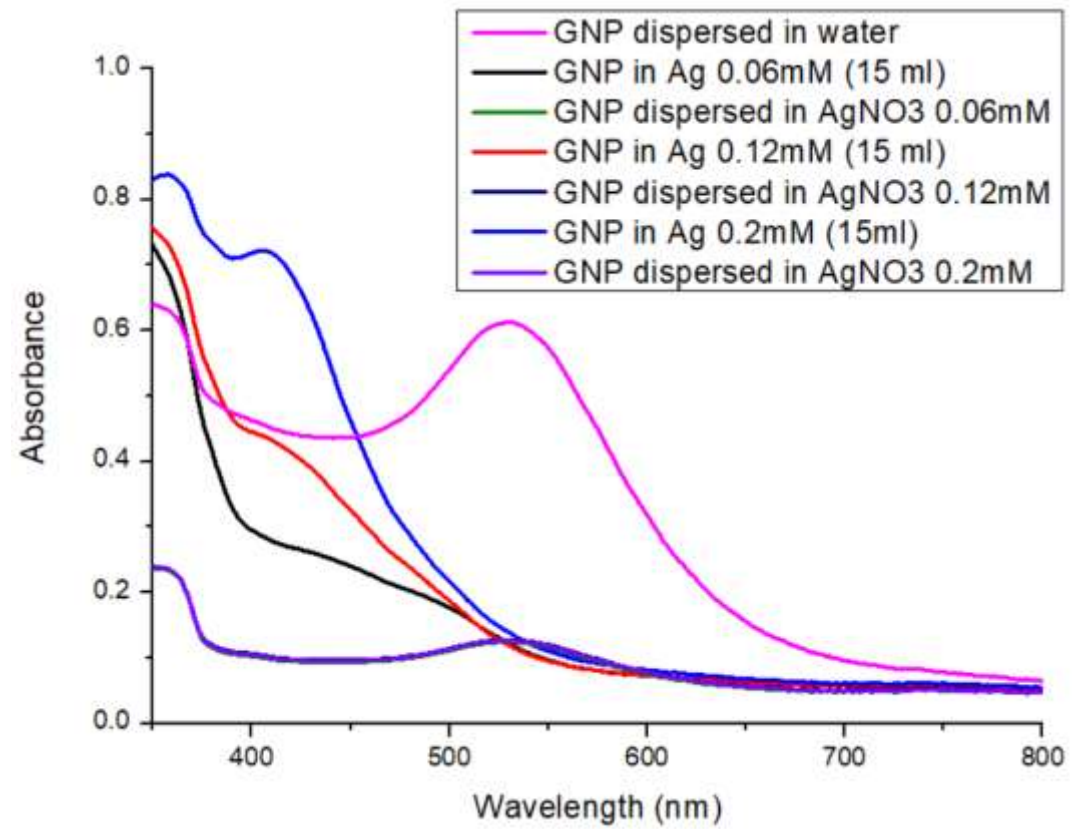
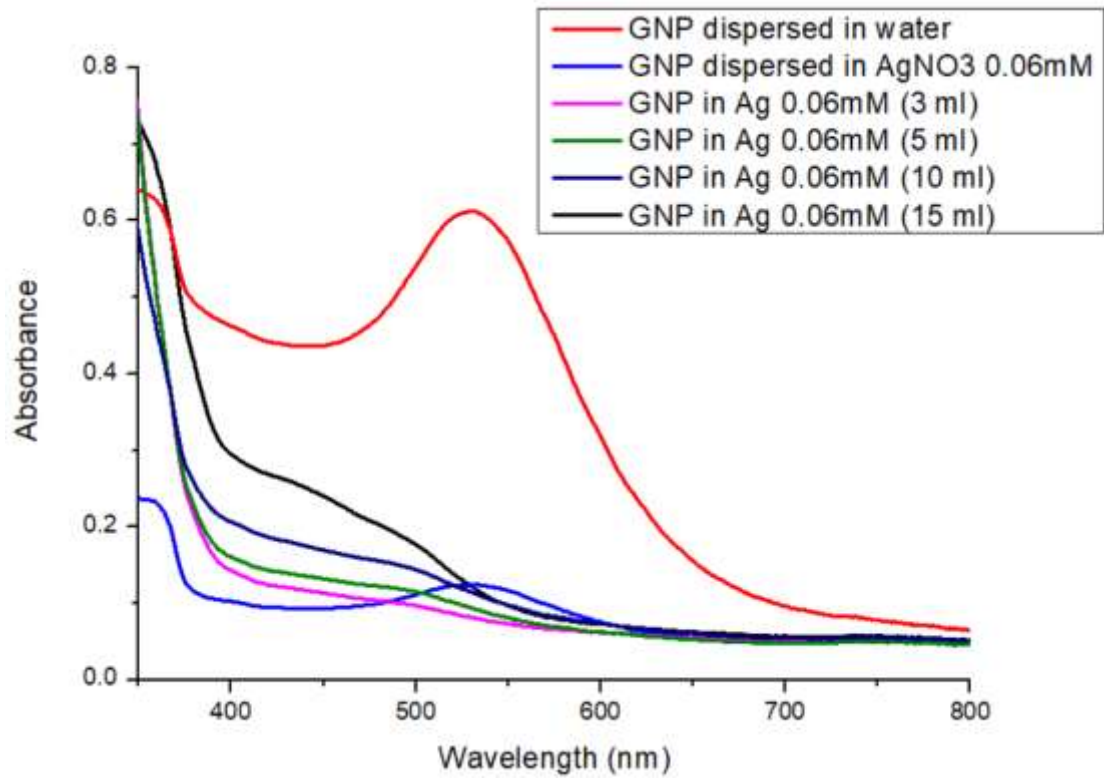




Experiment 5 : Centrifugation (Au core Ag shell)

- **GNP Samples** : 1.5 ml Centrifuged (TA 0.04mM)(9000 rpm 90 mins)
- **Silver Nitrate solution** : 0.06 mM (shell solution)
- Solutions are prepared with DI water.
- Each 1.5ml sample is made up to 9ml and dispersed in Ag salt solution and added to a pool of Tannic Acid (0.03mM – 15ml – pH 8)

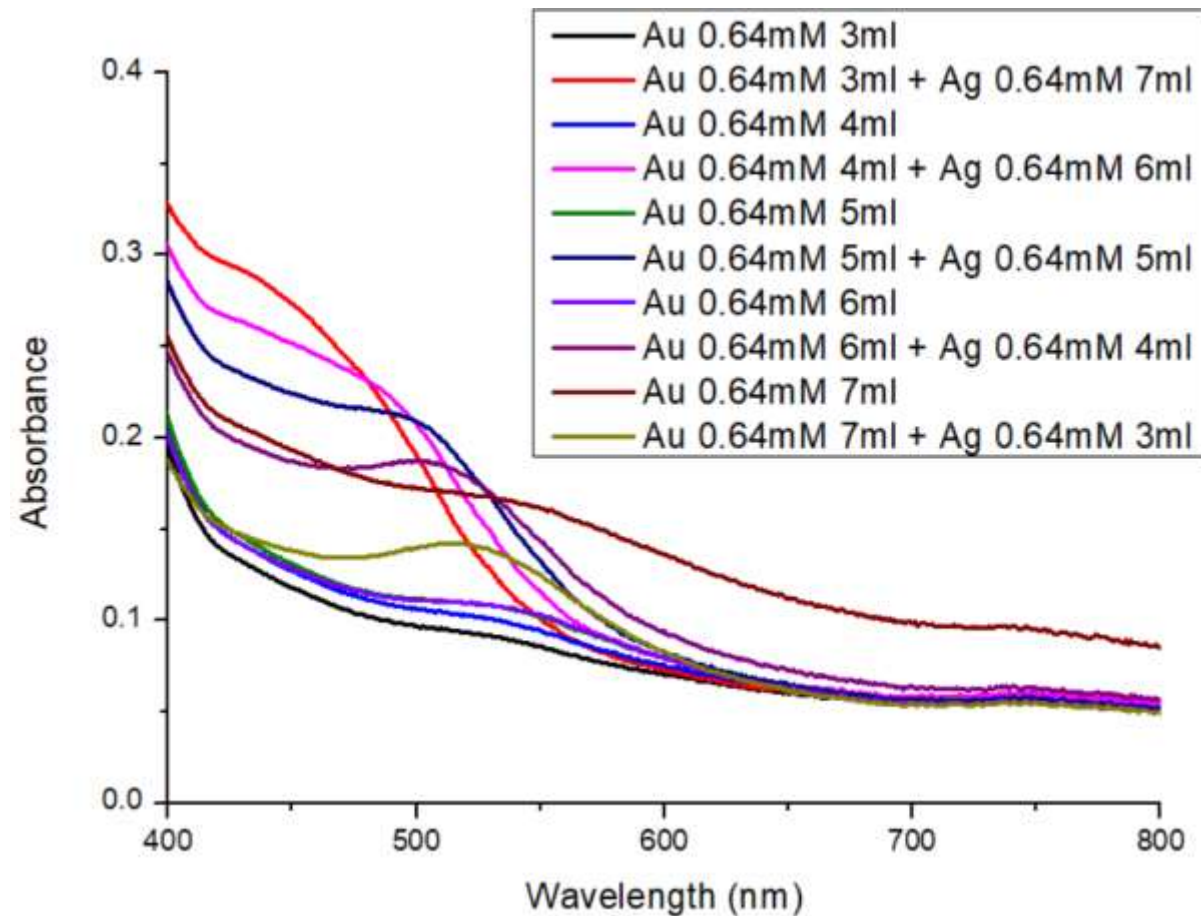
Impeller Rotation – 1000 rpm Silver Nitrate Solution : 0.06 mM					
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25					
Sample	Input mode	V of Gold Salt (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	0.06	3	8
2	Dropwise	10	0.06	5	7-8
3	Dropwise	10	0.06	10	7-8
4	Dropwise	10	0.06	15	7
5	Dropwise	10	0.12	15	7
6	Dropwise	10	0.2	15	7



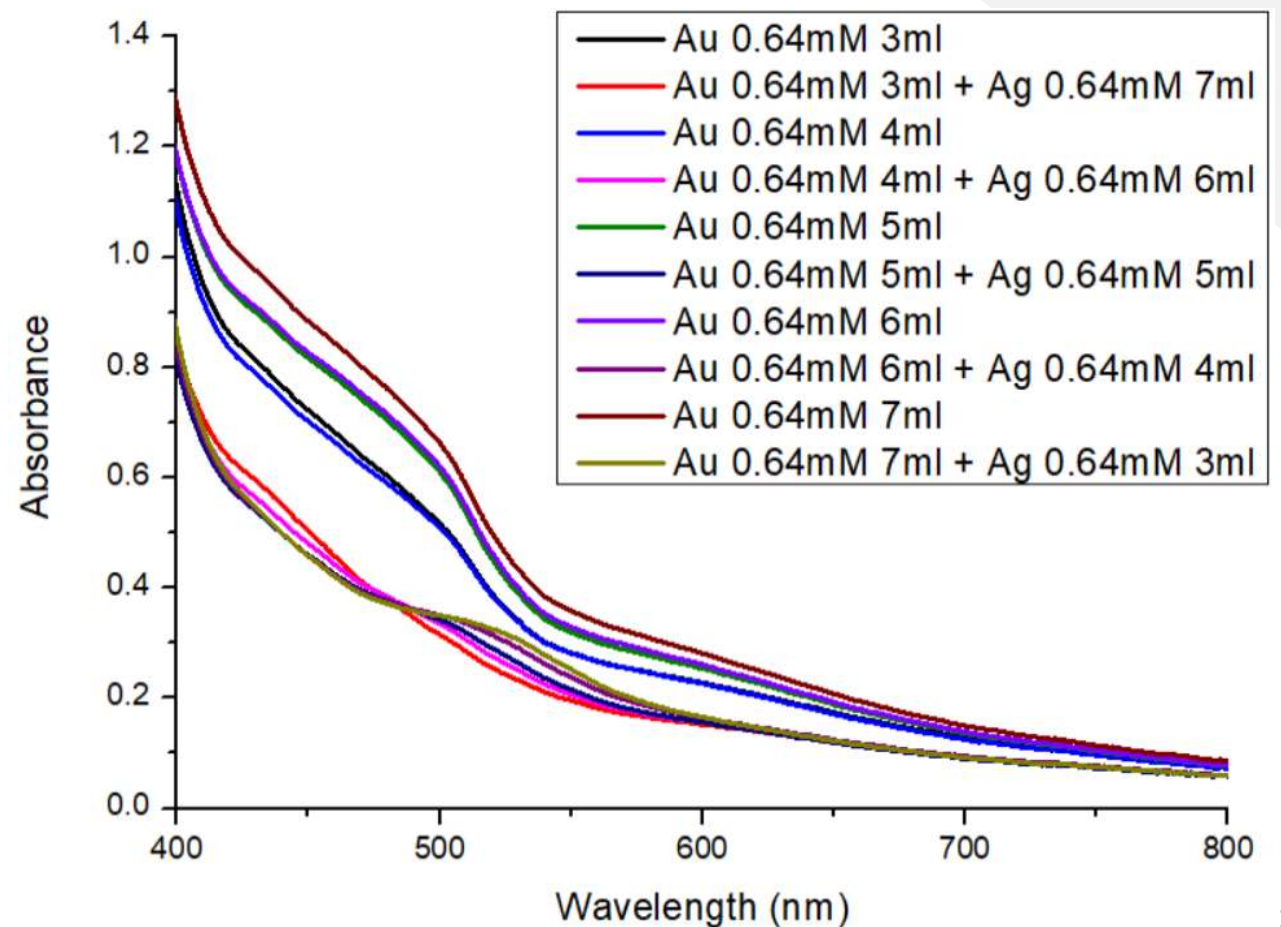
Experiment 6 : Combinations (Au core Ag shell)

- Chloroauric acid solution : 0.64mM
- Silver Nitrate solution : 0.64 mM
- Tannic Acid : 0.89mM | 0.15mM
- Solutions are prepared with DI water.

0.15mM Tannic Acid



0.89mM Tannic Acid



Core-Shell

Ag core – Au shell

- Dilution
- Without dilution

Experiment 7 : Dilution (Ag core Au shell)

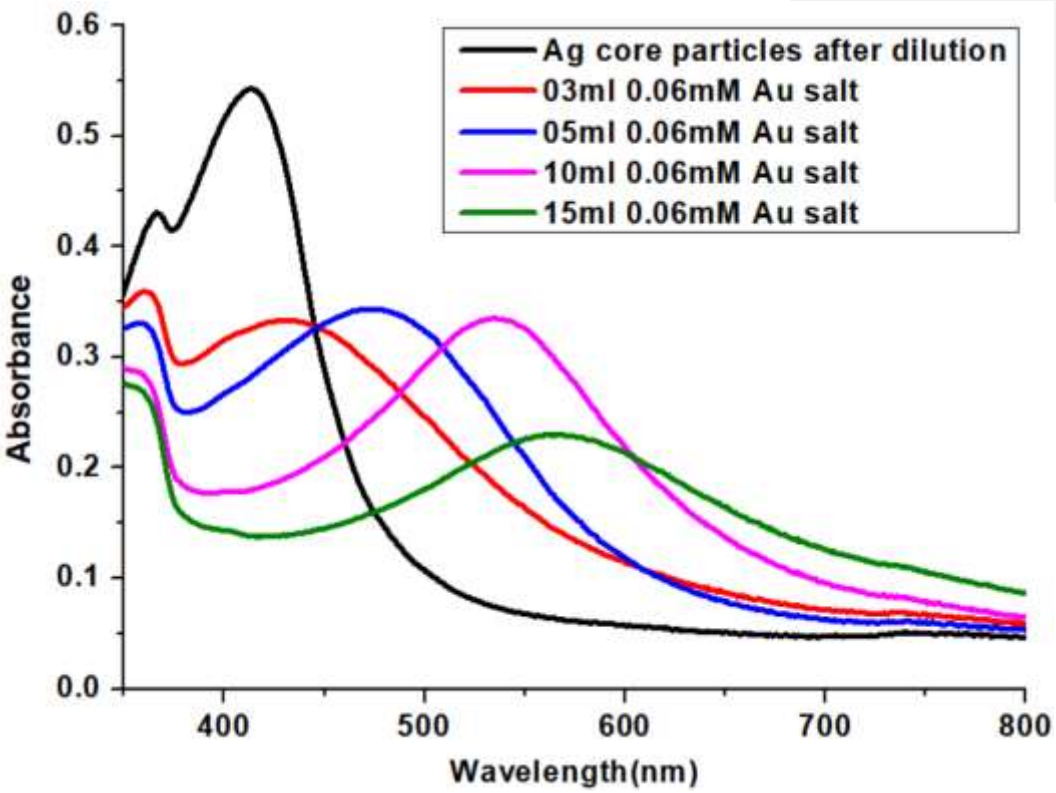
- **SNP Samples** : 2.5 ml made up to 15 ml (core solution)
- **Chloroauric acid solution** : 0.06 mM (shell solution)
- Solutions are prepared with DI water.
- pH is adjusted using 1 w/v of Potassium Carbonate solution
- 15 ml of SNP sample is taken in each beaker, gold salt solution is added

1) Without change in pH of core solution

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sampl e	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	10	6 - 7
2	Dropwise	10	15	0.06	15	6 – 7
3	Dropwise	10	15	0.06	20	6
4	Dropwise	10	15	0.06	25	6

2) pH of core solution adjusted to 10 – trial I

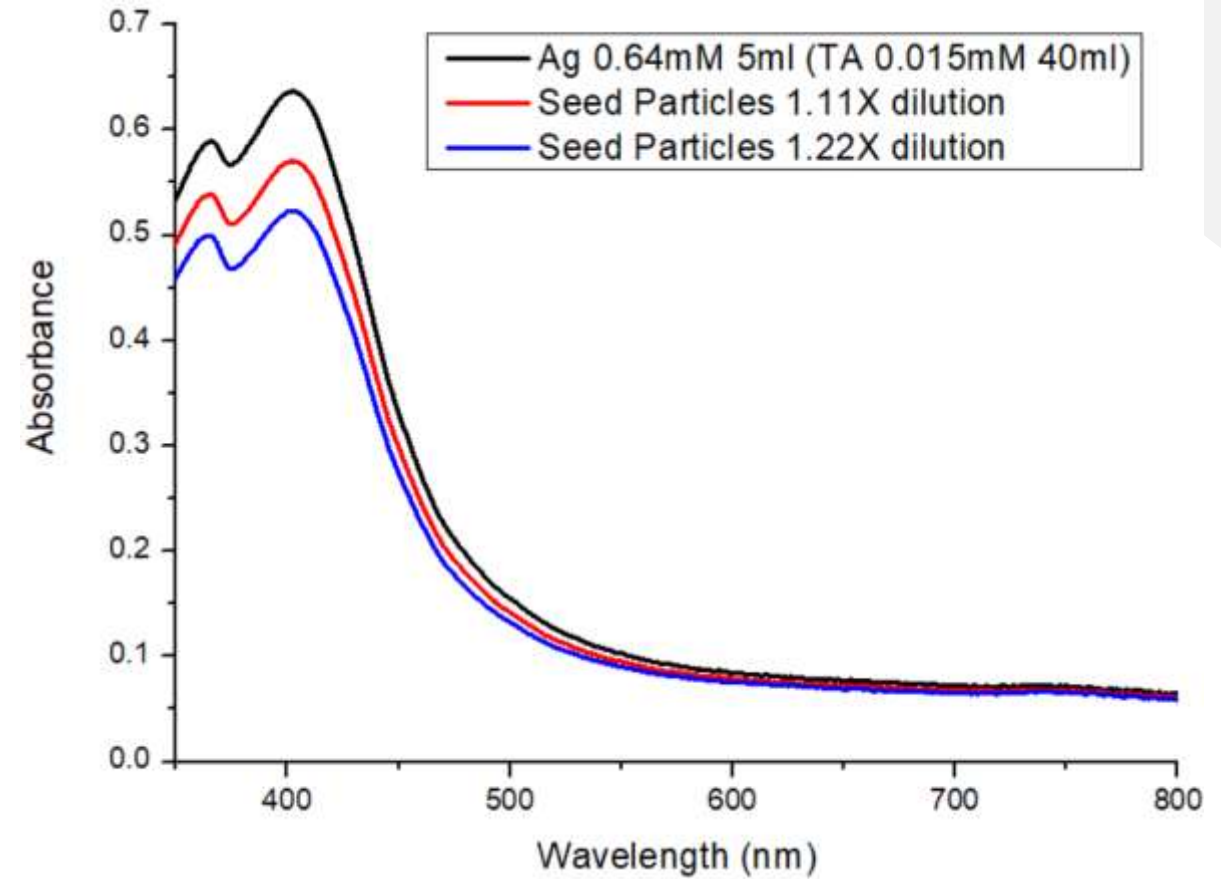
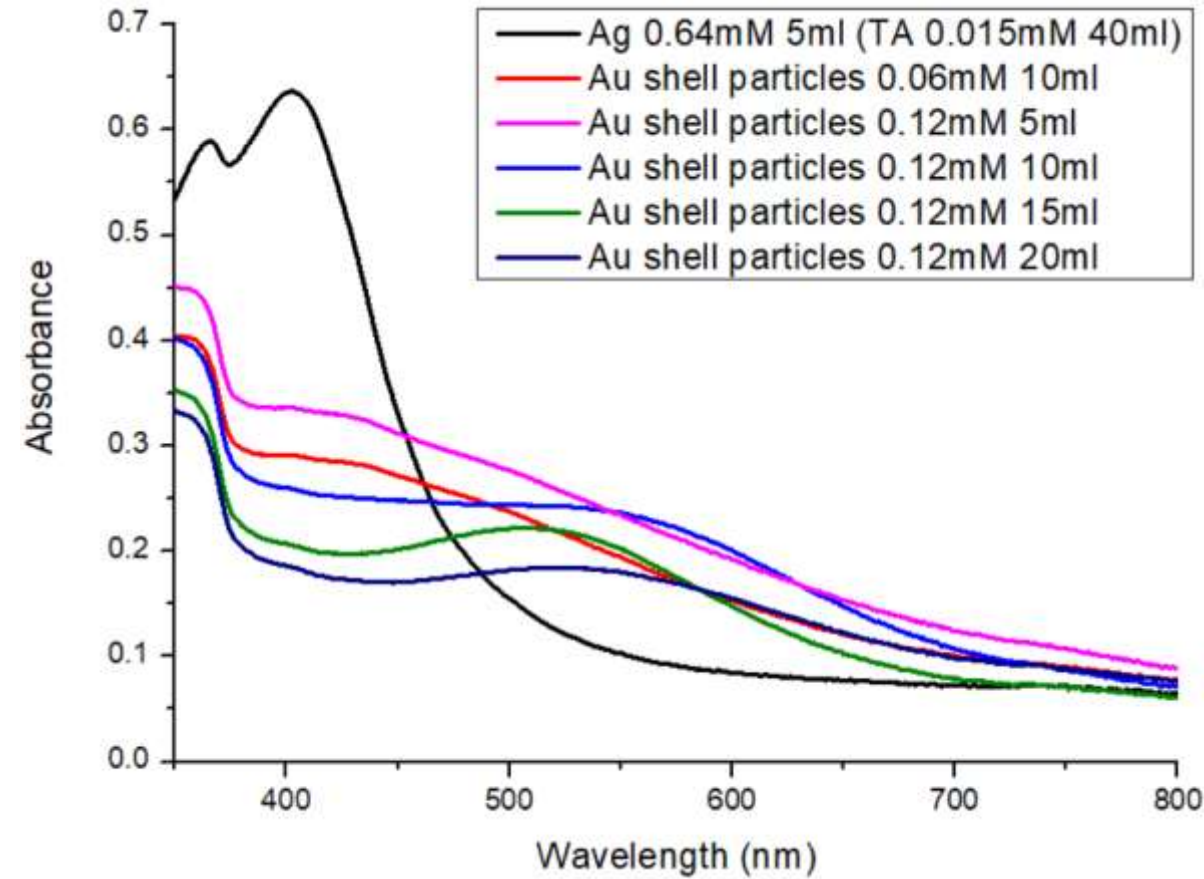
Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sampl e	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	3	7 - 8
2	Dropwise	10	15	0.06	5	7
3	Dropwise	10	15	0.06	10	7
4	Dropwise	10	15	0.06	15	7

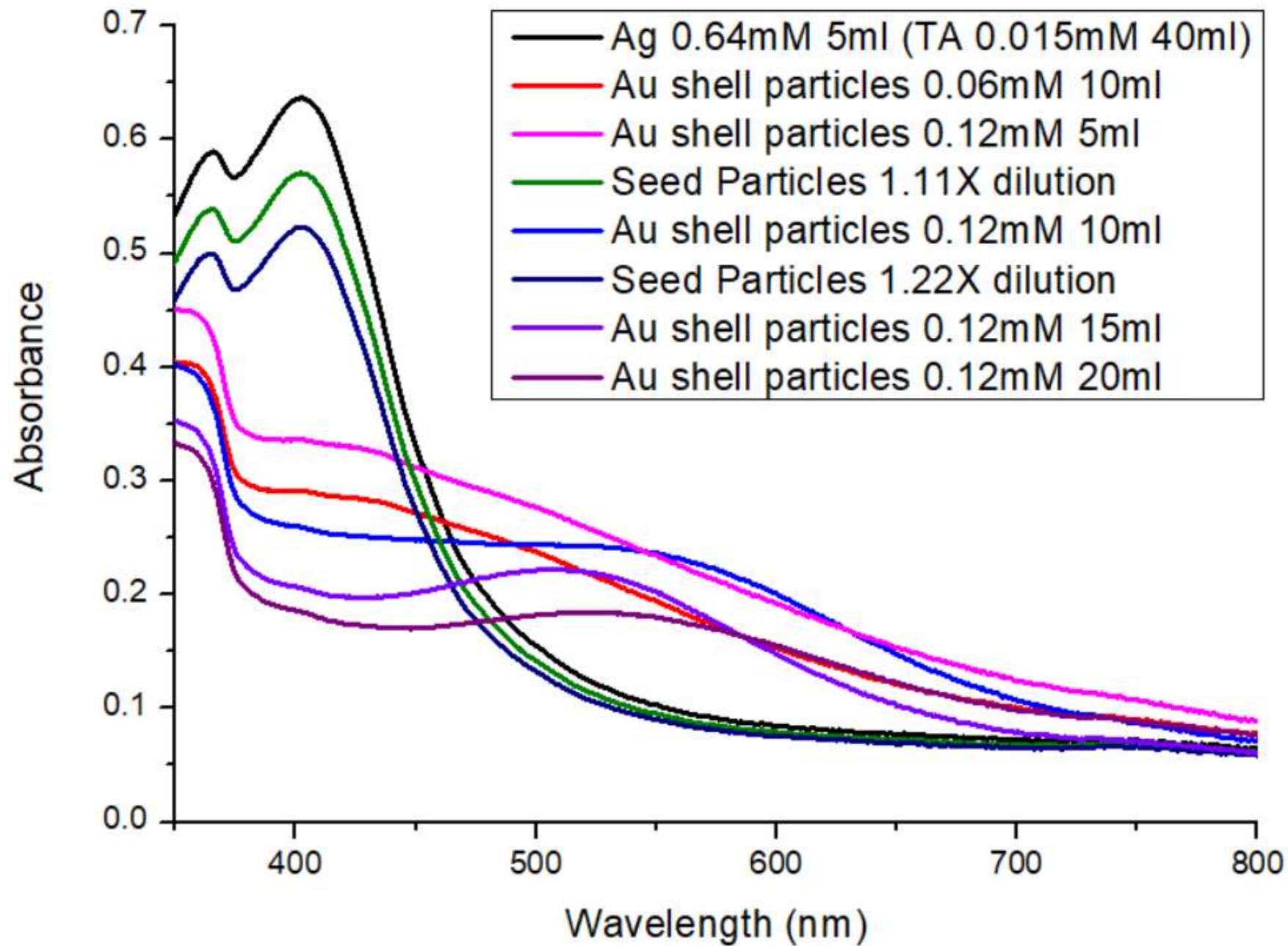


Experiment 8 : No dilution (Ag core Au shell)

- **SNP Samples** : 15ml (core solution : no dilution) (TA 0.015mM)
- **Chloroauric acid solution** : 0.06 mM | 0.12 mM(shell solution)
- Solutions are prepared with DI water.
- pH is adjusted using 1 w/v of Potassium Carbonate solution
- 15 ml of SNP sample is taken in each beaker, gold salt solution is added

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM & 0.12 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	5	15	0.06	10	7-8
2	Dropwise	5	15	0.12	5	7-8
3	Dropwise	5	15	0.12	10	7
4	Dropwise	5	15	0.12	15	7
5	Dropwise	5	15	0.12	20	7





Continuous

Synthesis

- GNP
- SNP
- Ag core Au shell

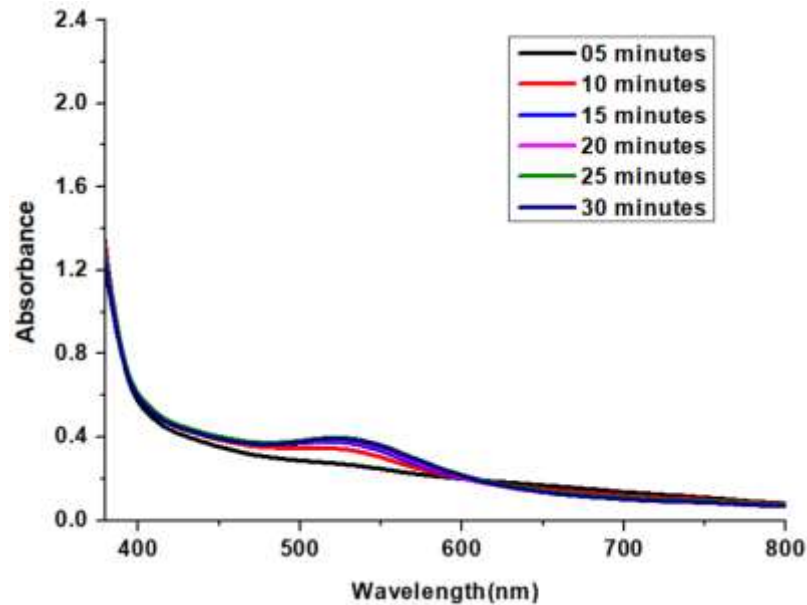
Set-up



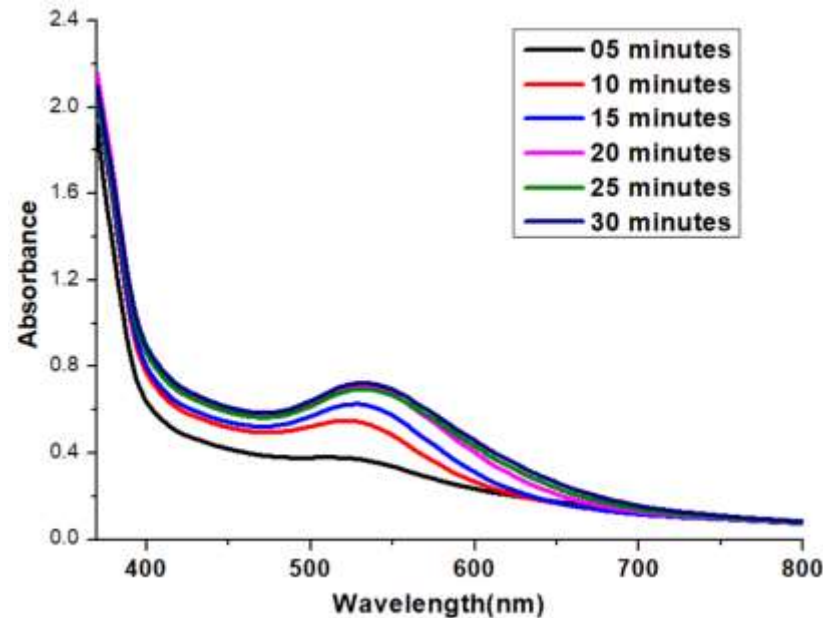
Experiment 1 : Fabrication of GNP

- **Tannic Acid solution** : 1.2mM. pH adjusted to 10 by using 10 w/v of Potassium Carbonate solution.
- **Chloroauric Acid solution** : I) 1.2mM II) 2.4mM III) 3.6mM
- Solutions are prepared with DI water.
- Flow rates : Tannic Acid – 6 ml/min
Chloroauric Acid – 10 ml/min
- Samples are collected for 5 minutes each.

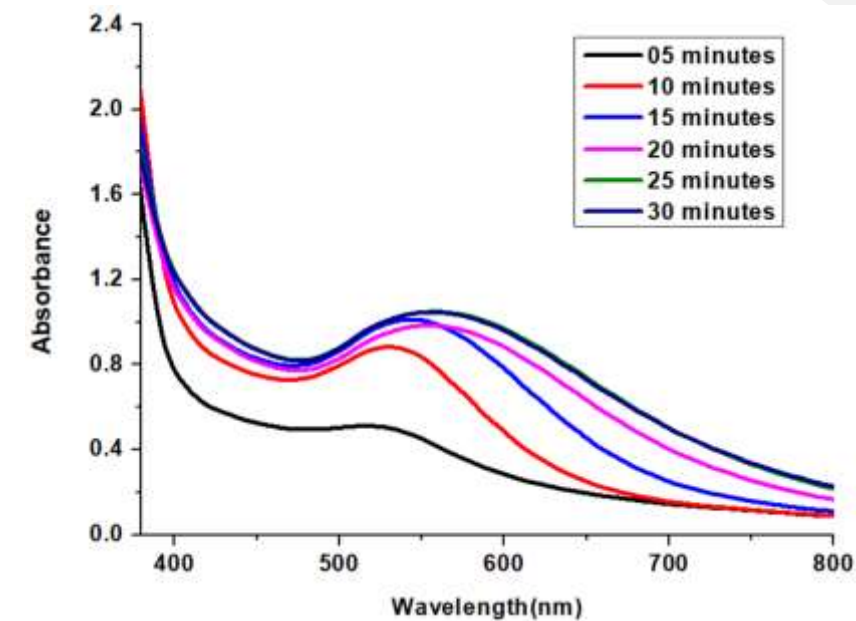
1.2 mM Au Salt – 141.42 mg Au/hr



2.4 mM Au Salt – 282.84 mg Au/hr



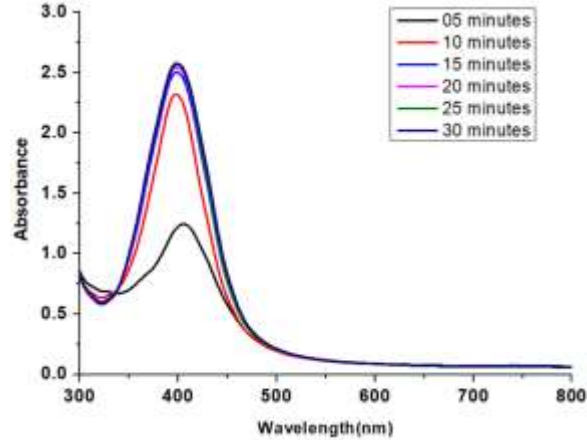
3.6 mM Au Salt – 424.26 mg Au/hr



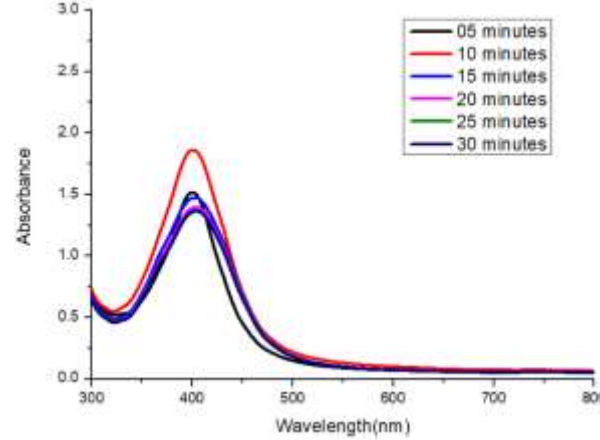
Experiment 2 : Fabrication of SNP

- **Tannic Acid solution** : 0.03 mM. pH adjusted to 8 by using 10 w/v of Potassium Carbonate solution.
- **Silver Nitrate solution** : I) 1.2 mM II) 2.4 mM III) 3.6 mM IV) 4.8 mM V) 6mM
- Solutions are prepared with DI water.
- Flow rates : Tannic Acid – 6 ml/min
Silver Nitrate – 10 ml/min
- Samples are collected for 5 minutes each.

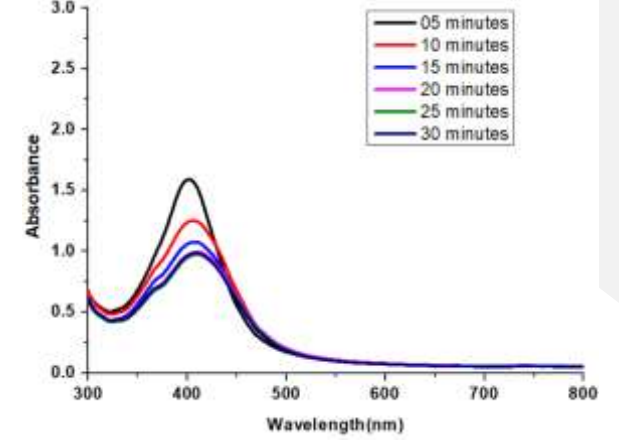
1.2 mM Ag Salt – 77.76 mg Ag/hr



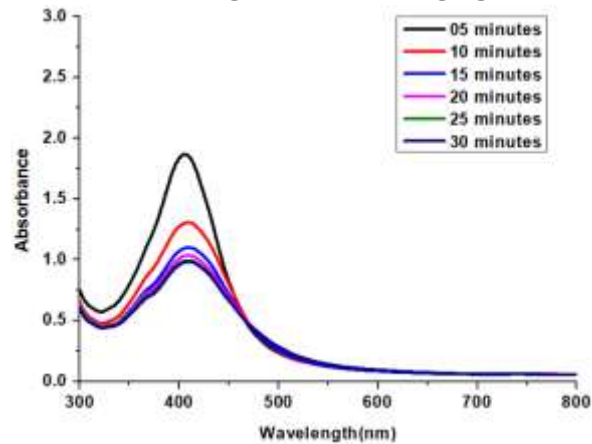
2.4 mM Ag Salt – 155.52 mg Ag/hr



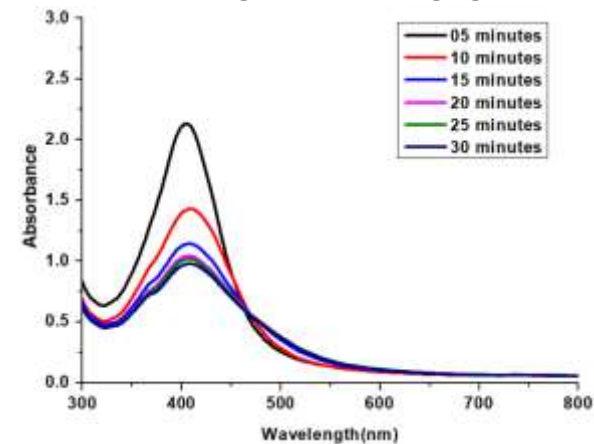
3.6 mM Ag Salt – 233.28 mg Ag/hr



4.8 mM Ag Salt – 311.04 mg Ag/hr

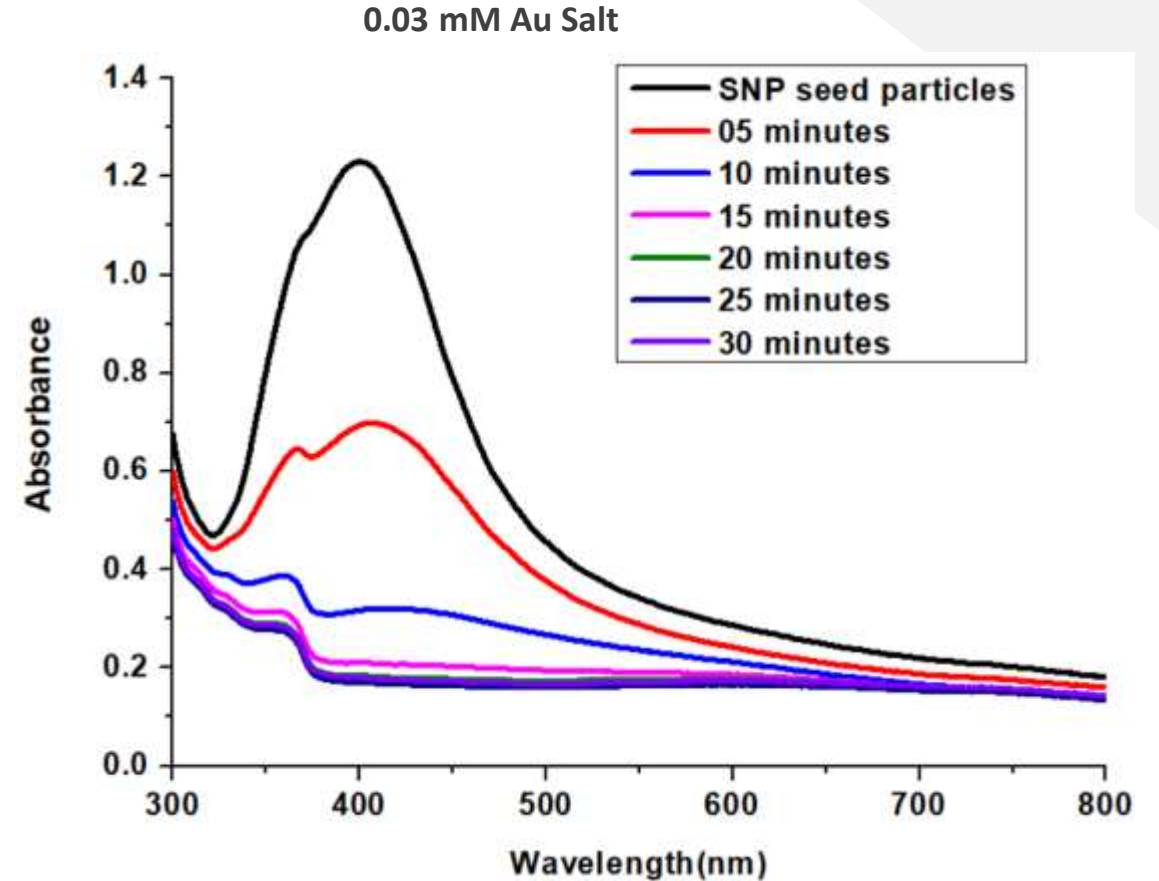
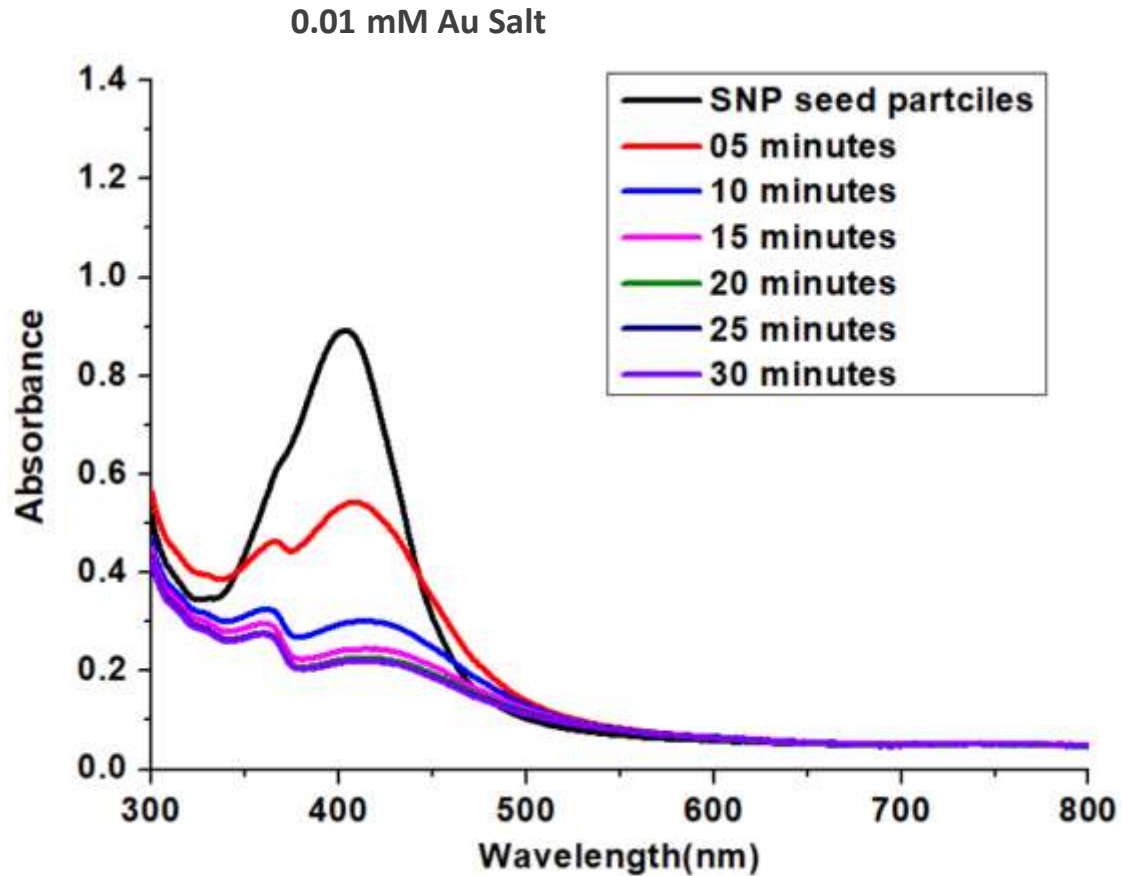


6 mM Ag Salt – 388.8 mg Ag/hr



Experiment 3 : Ag core – Au shell

- **SNP Sample** : 1.2mM Ag, diluted 6 times and pH adjusted to 10 using 10 w/v Potassium Carbonate solution.
- **Chloroauric Acid solution** : I) 0.01 mM II) 0.03 mM
- Solutions are prepared with DI water.
- Flow rates : SNP Sample – 6 ml/min
Chloroauric Acid – 10 ml/min
- Samples are collected for 5 minutes each.



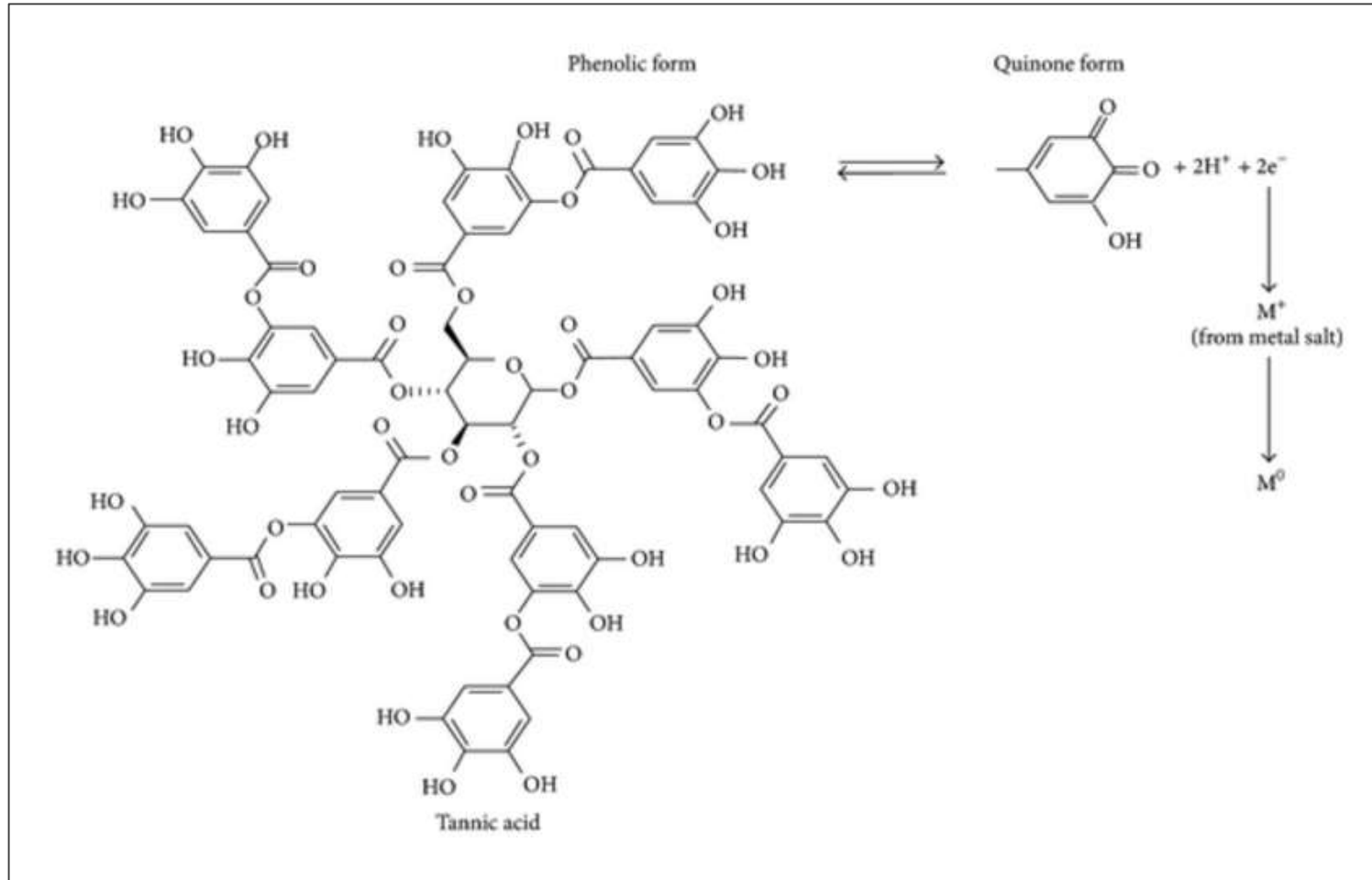


Thank You

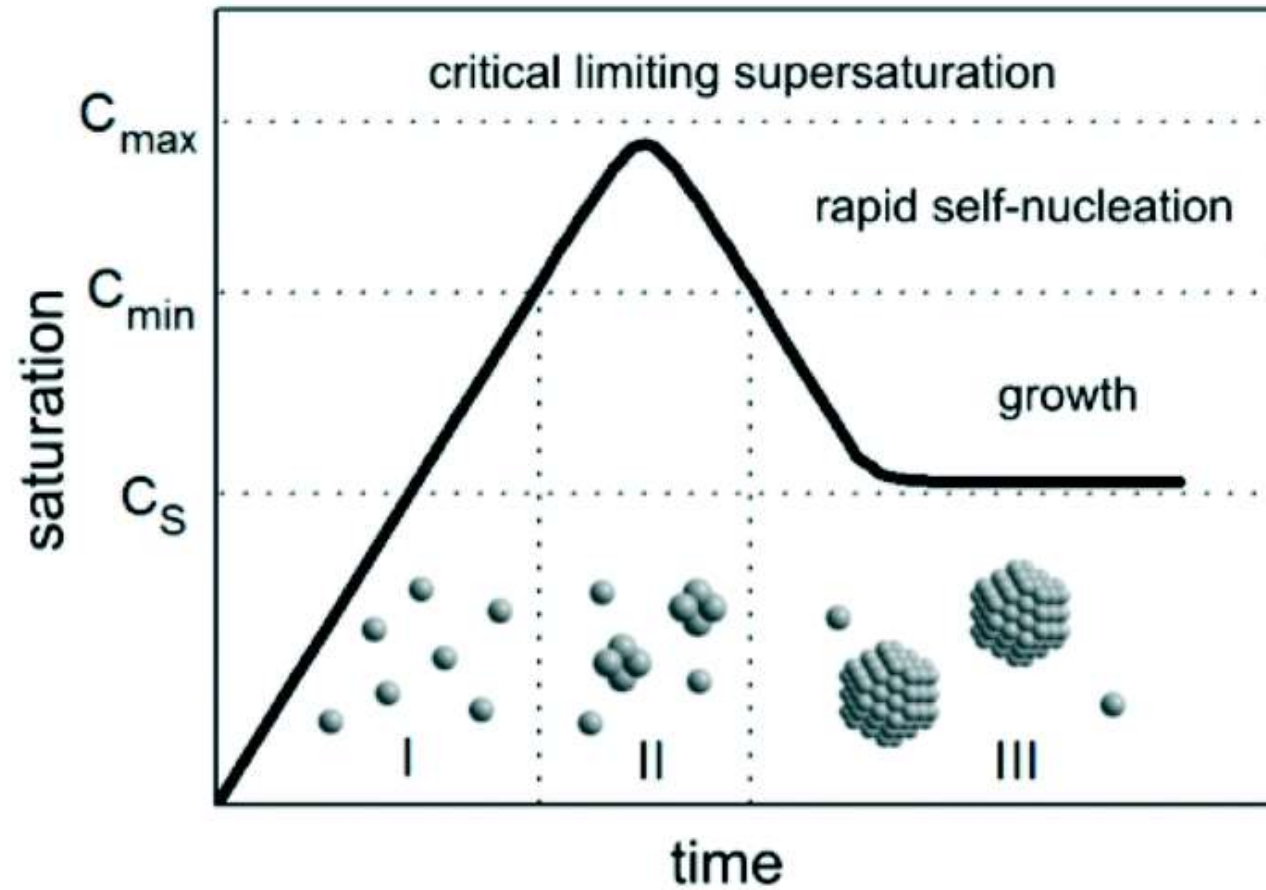


Tannic Acid behavior

Tannic acid is a specific form of tannin, a type of polyphenol. Its weak acidity (pK_a around 6) is due to the numerous phenol groups in the structure. The chemical formula for commercial tannic acid is often given as $C_{76}H_{52}O_{46}$



LaMer Model



The process can be divided into 3 basic stages I, II and III as mentioned in graph.

Stage I) Generation Stage

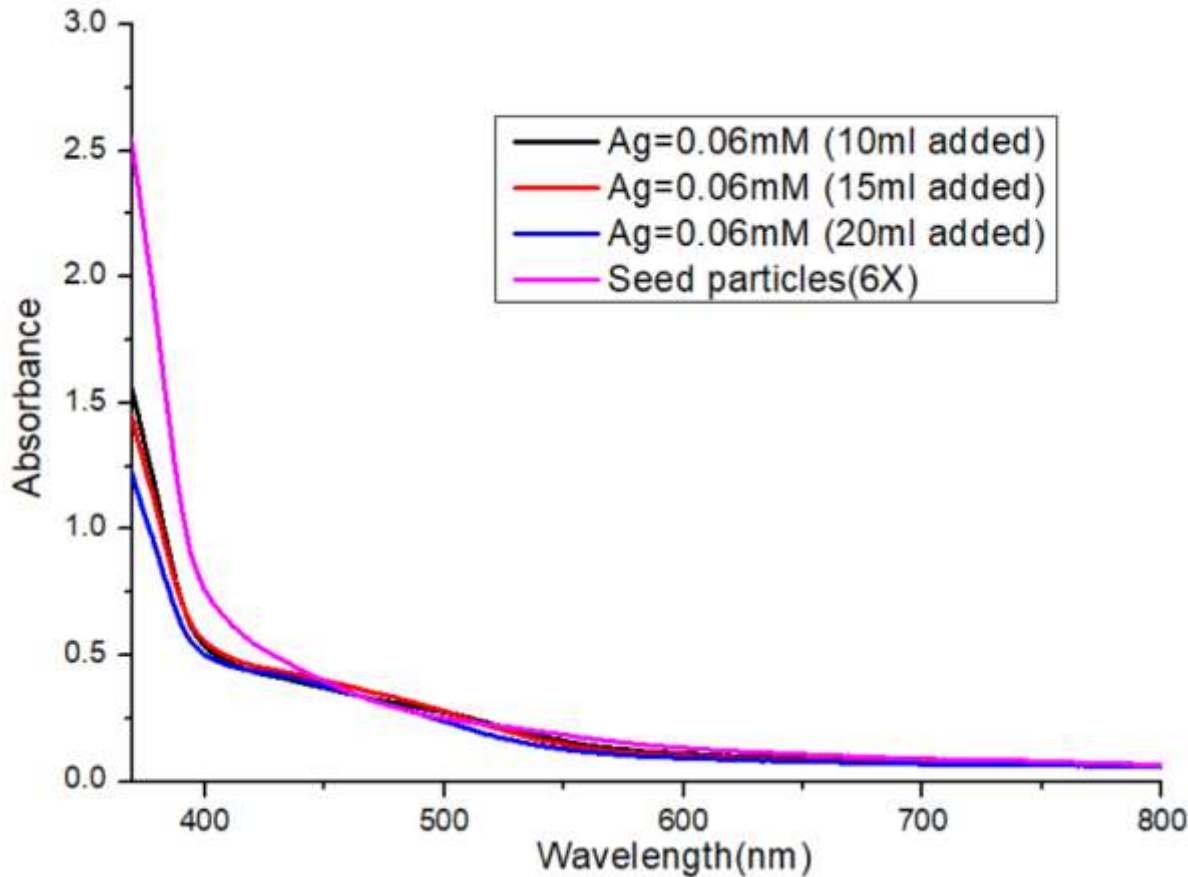
Stage II) Nucleation

Stage III) Growth

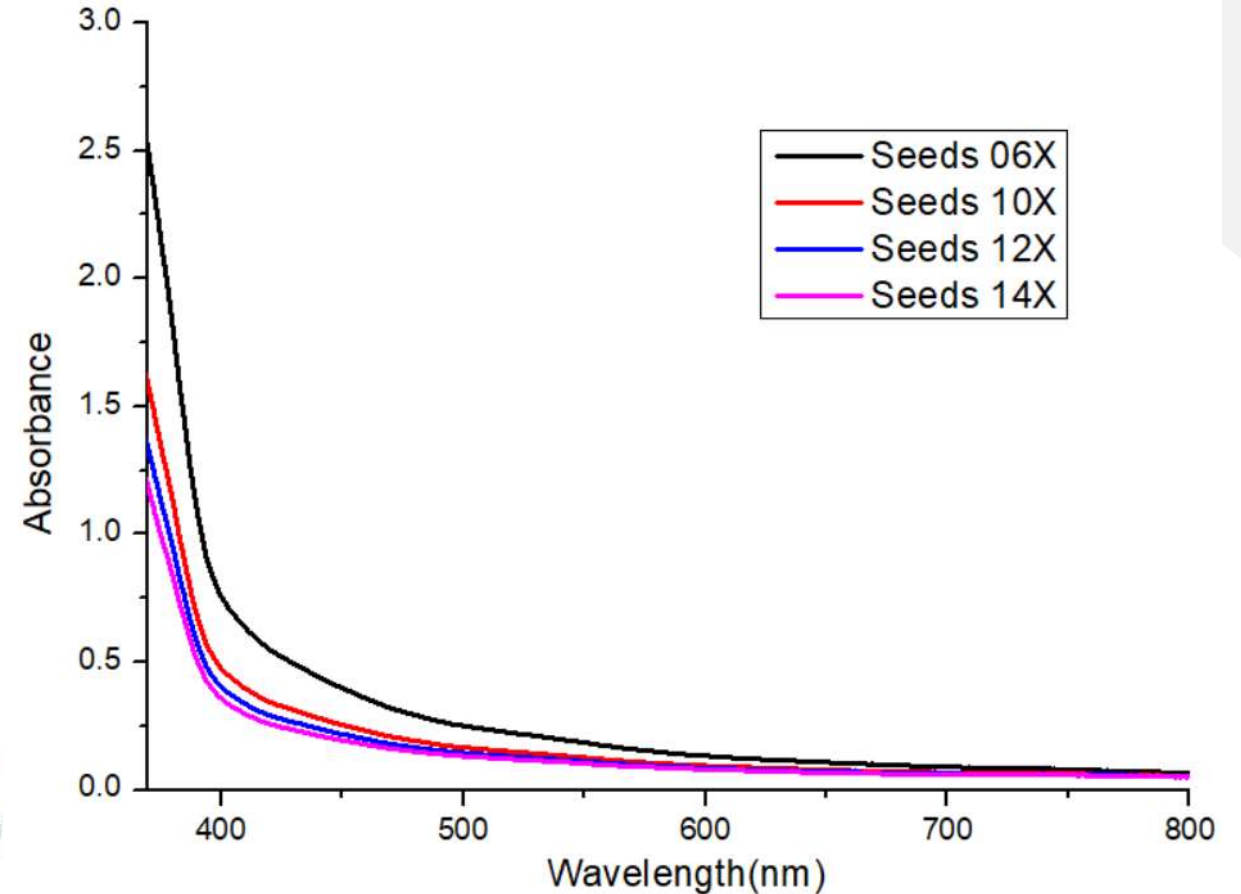
Experiment 3 : Core – Shell Particles - I

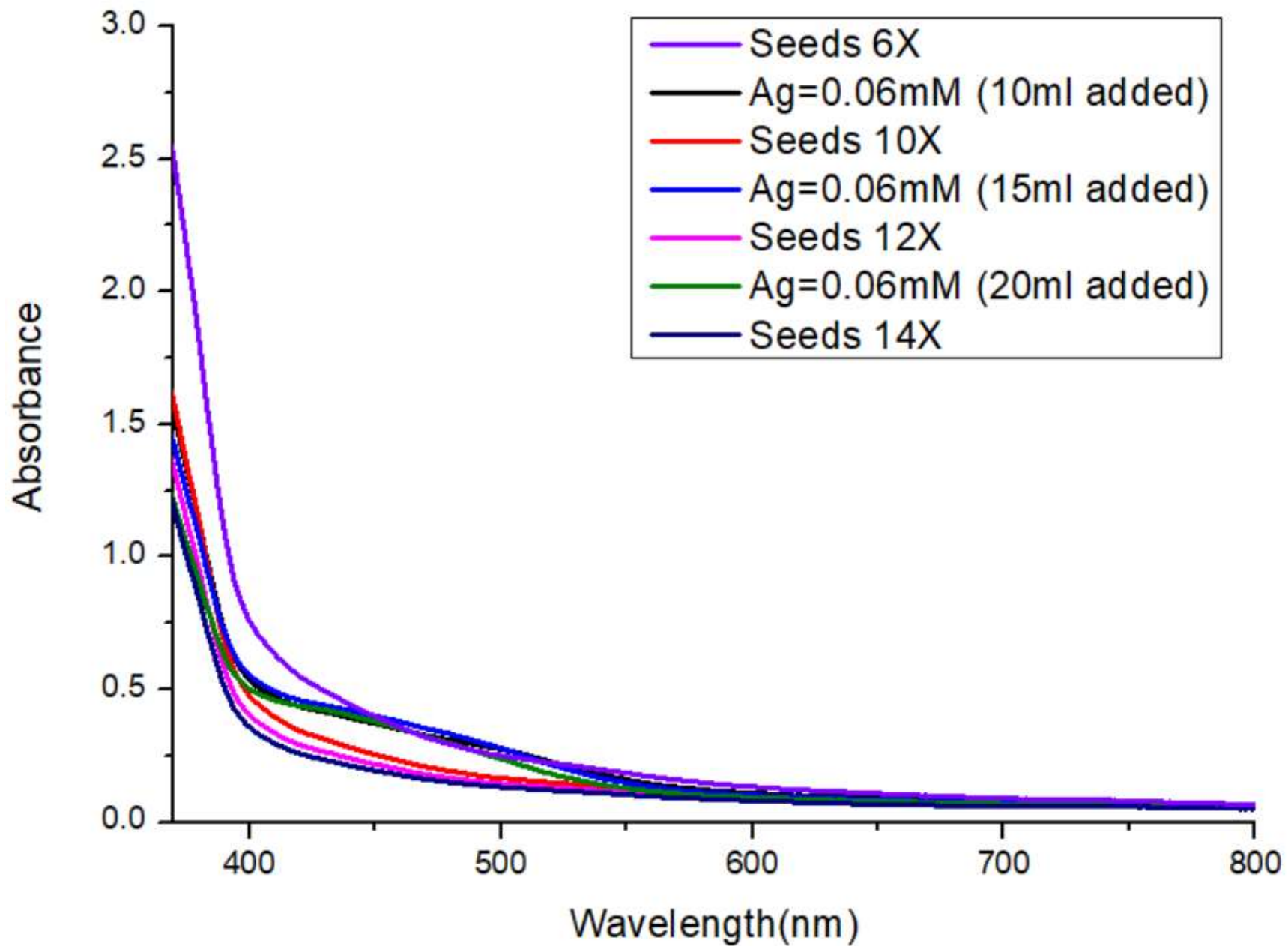
(Au core, Ag Shell) Trial 2

- **GNP Sample** : 2.5ml made up to 15 ml (core solution)
- **Silver Nitrate solution** : 0.06 mM (shell solution)
- Solutions are prepared with DI water.
- 15 ml of GNP sample is taken in 3 beakers, silver salt solution is added (K₂CO₃ 10w/v)



Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	10	7
2	Dropwise	10	15	0.06	15	7
3	Dropwise	10	15	0.06	20	7

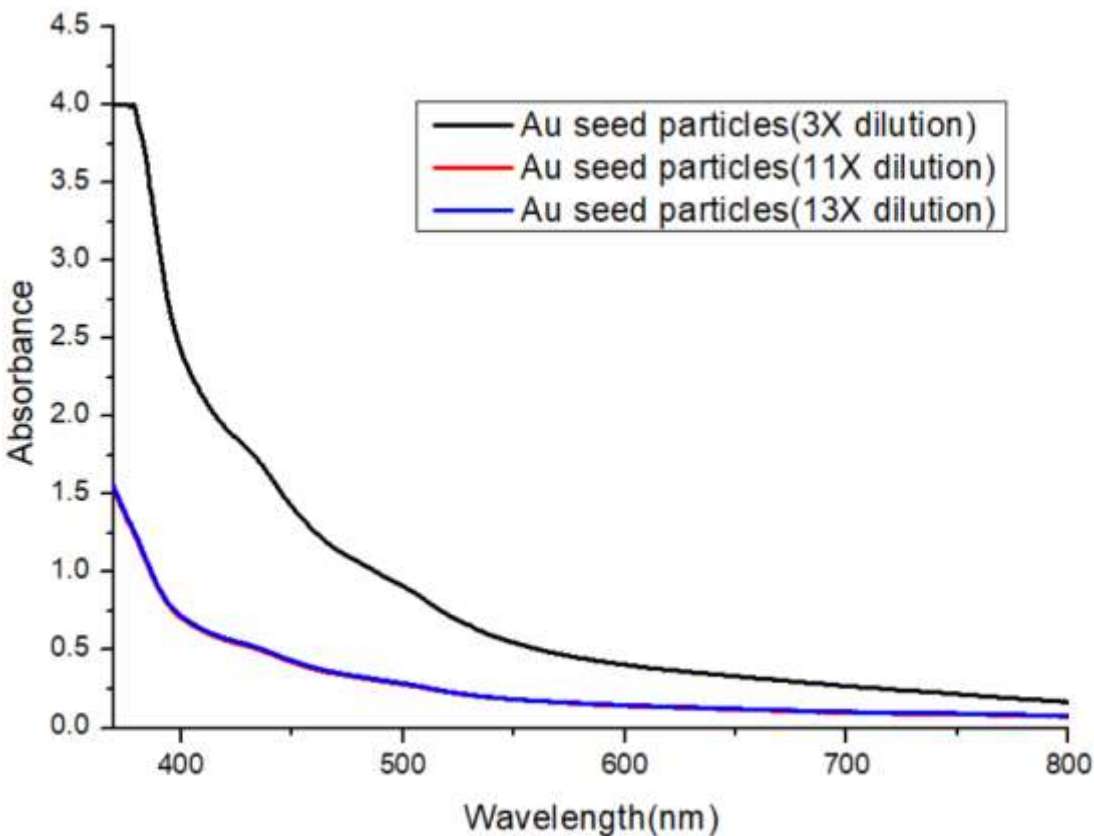




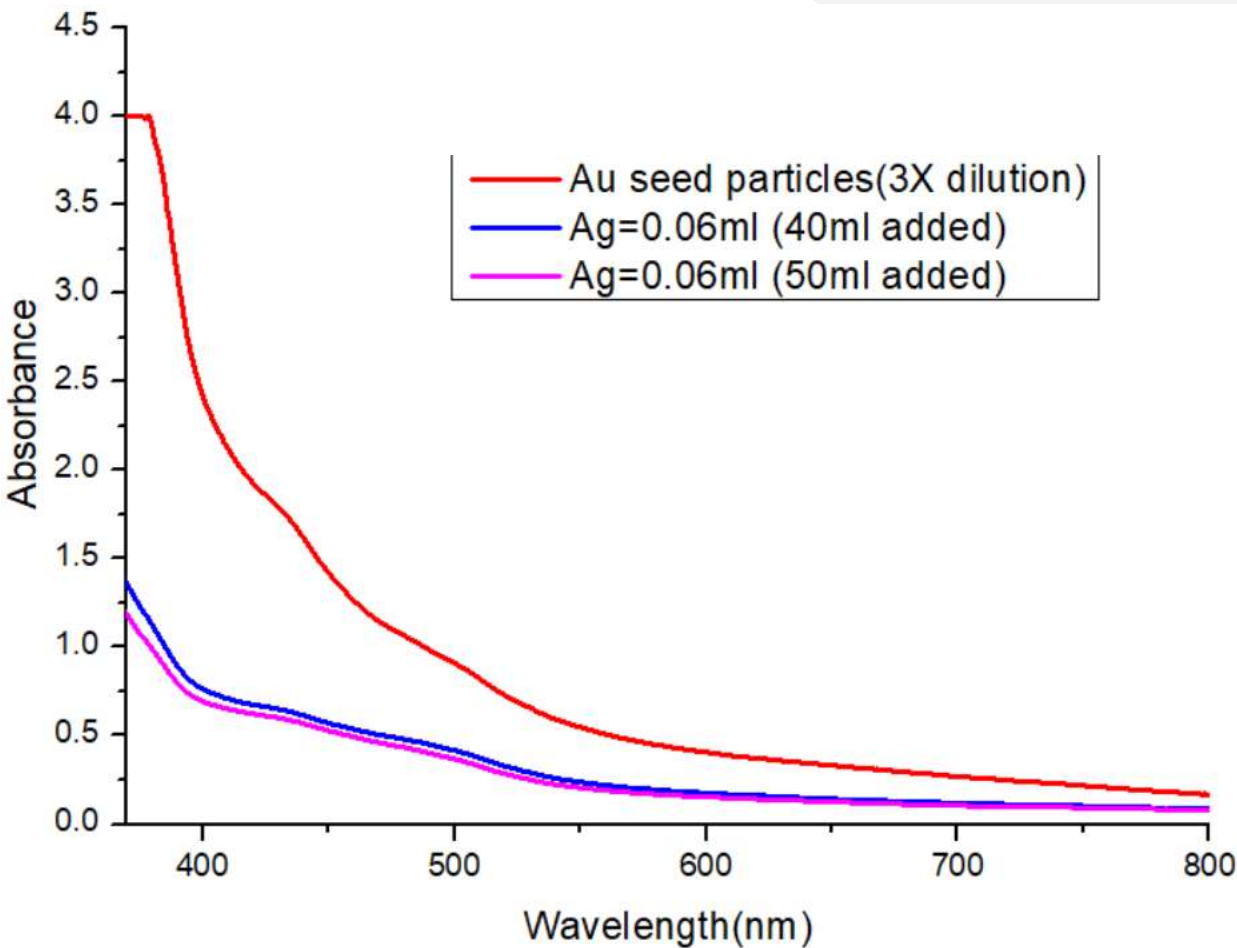
Experiment 3 : Core – Shell Particles - I

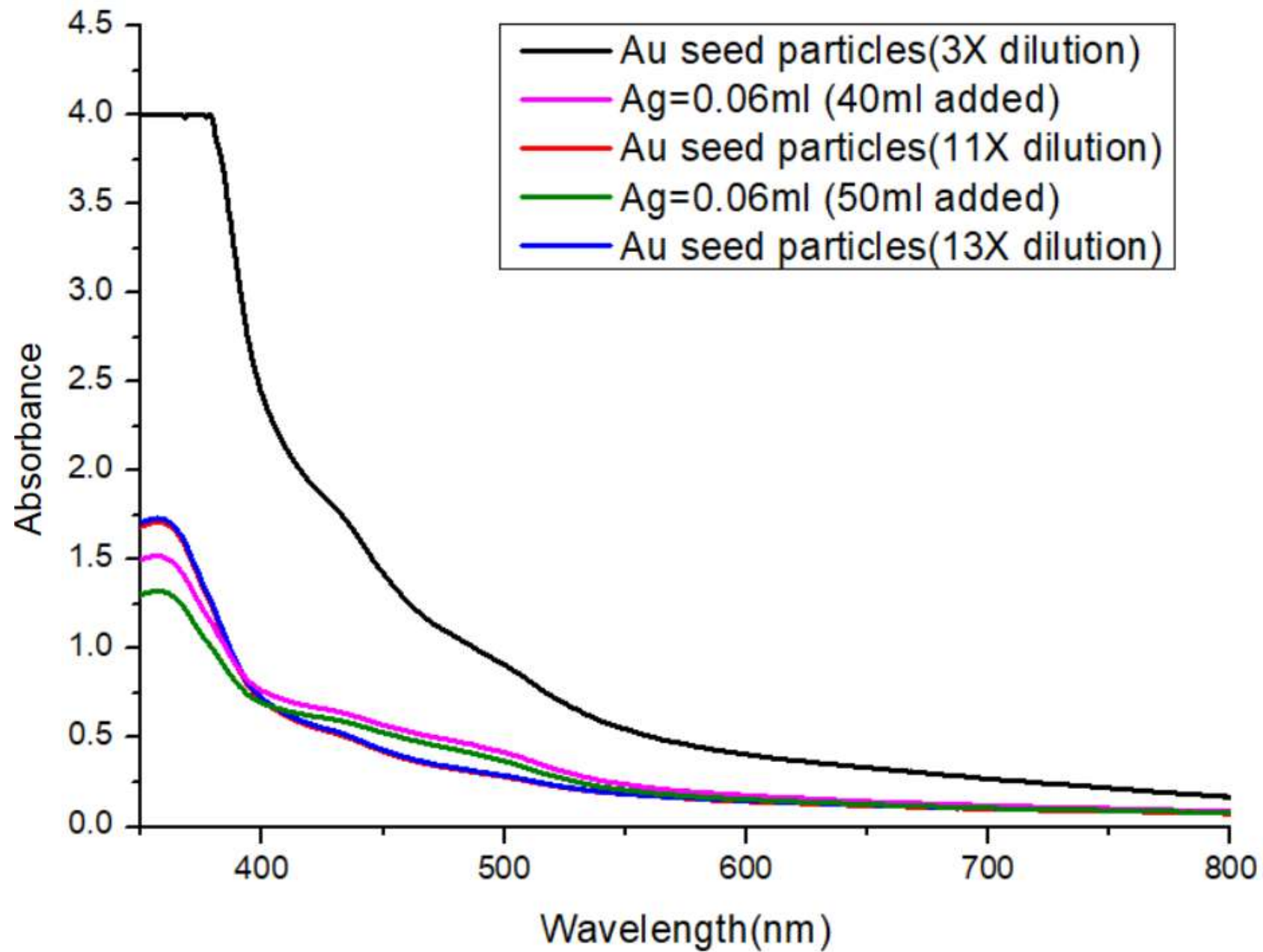
(Au core, Ag Shell) Trial 3

- **GNP Sample** : 5ml made up to 15 ml (core solution)
- **Silver Nitrate solution** : 0.06 mM (shell solution)
- Solutions are prepared with DI water.
- 15 ml of GNP sample is taken in 2 beakers, silver salt solution is added



Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	40	7
2	Dropwise	10	15	0.06	50	7





Experiment 3 : Core – Shell Particles - I

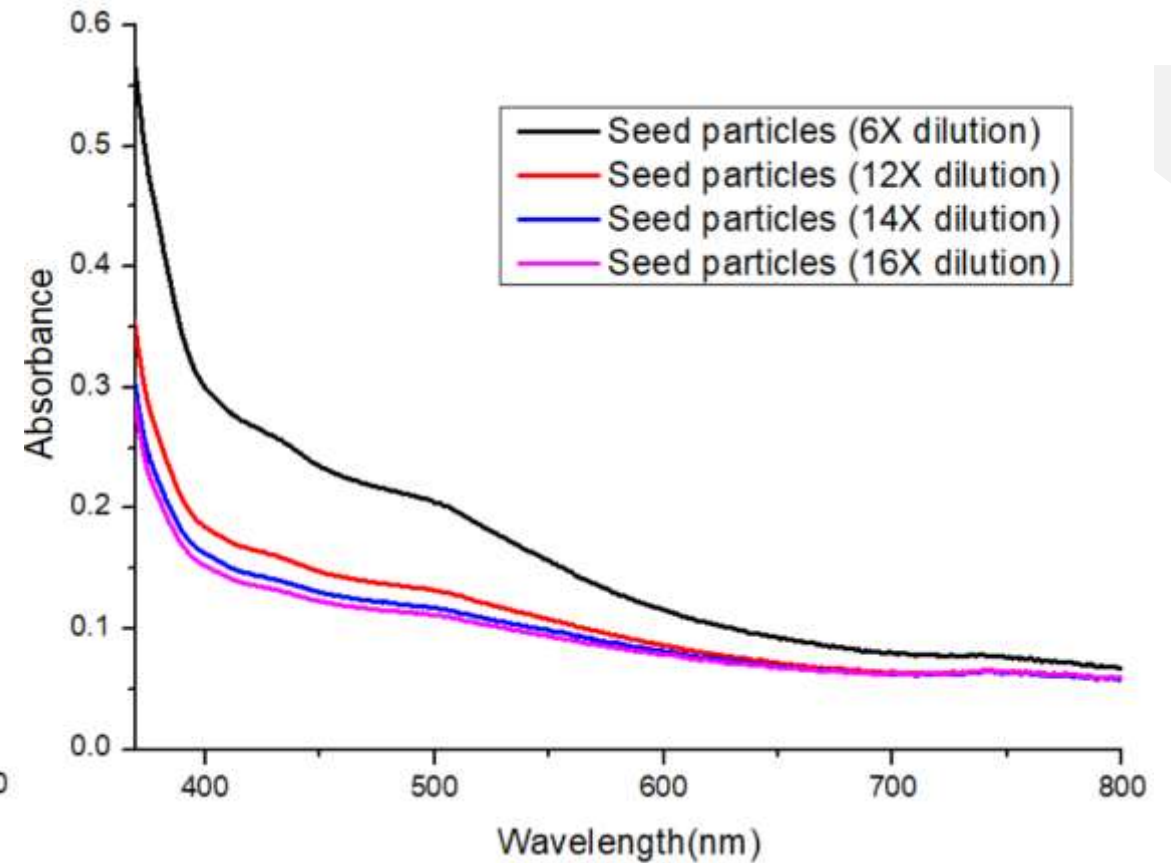
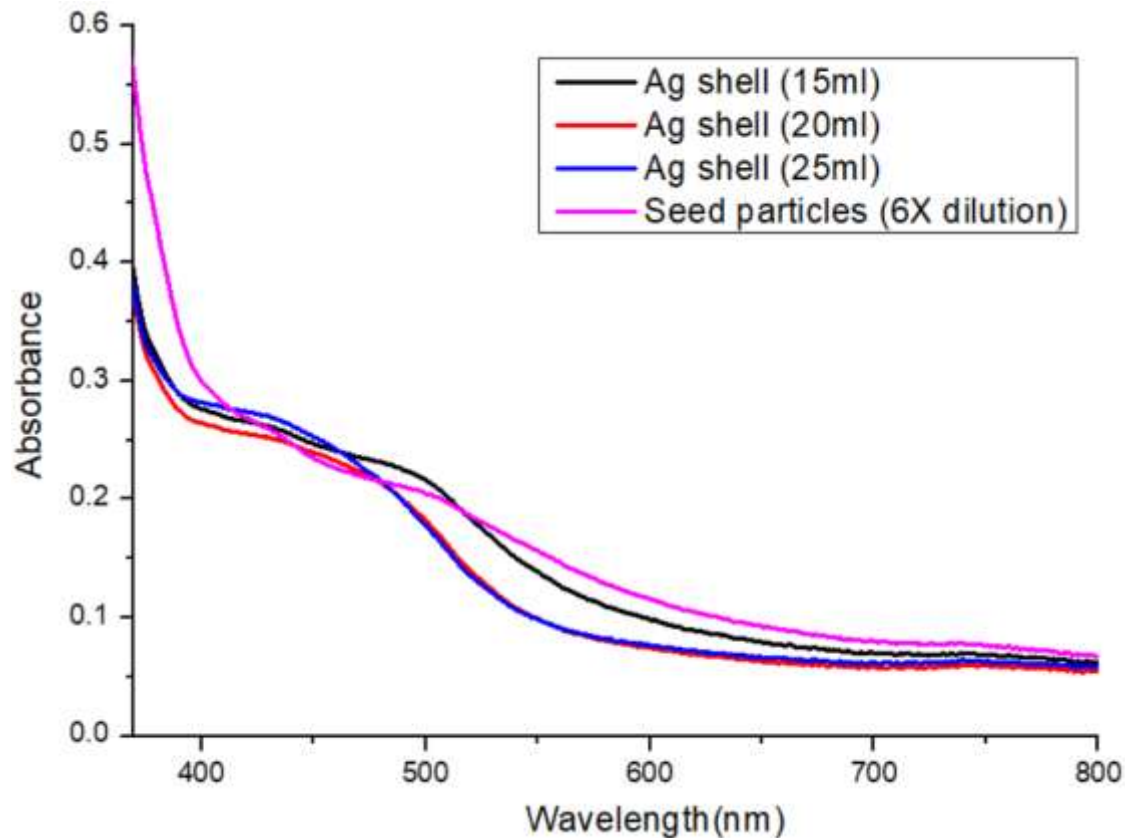
(Au core, Ag Shell) Trial 4

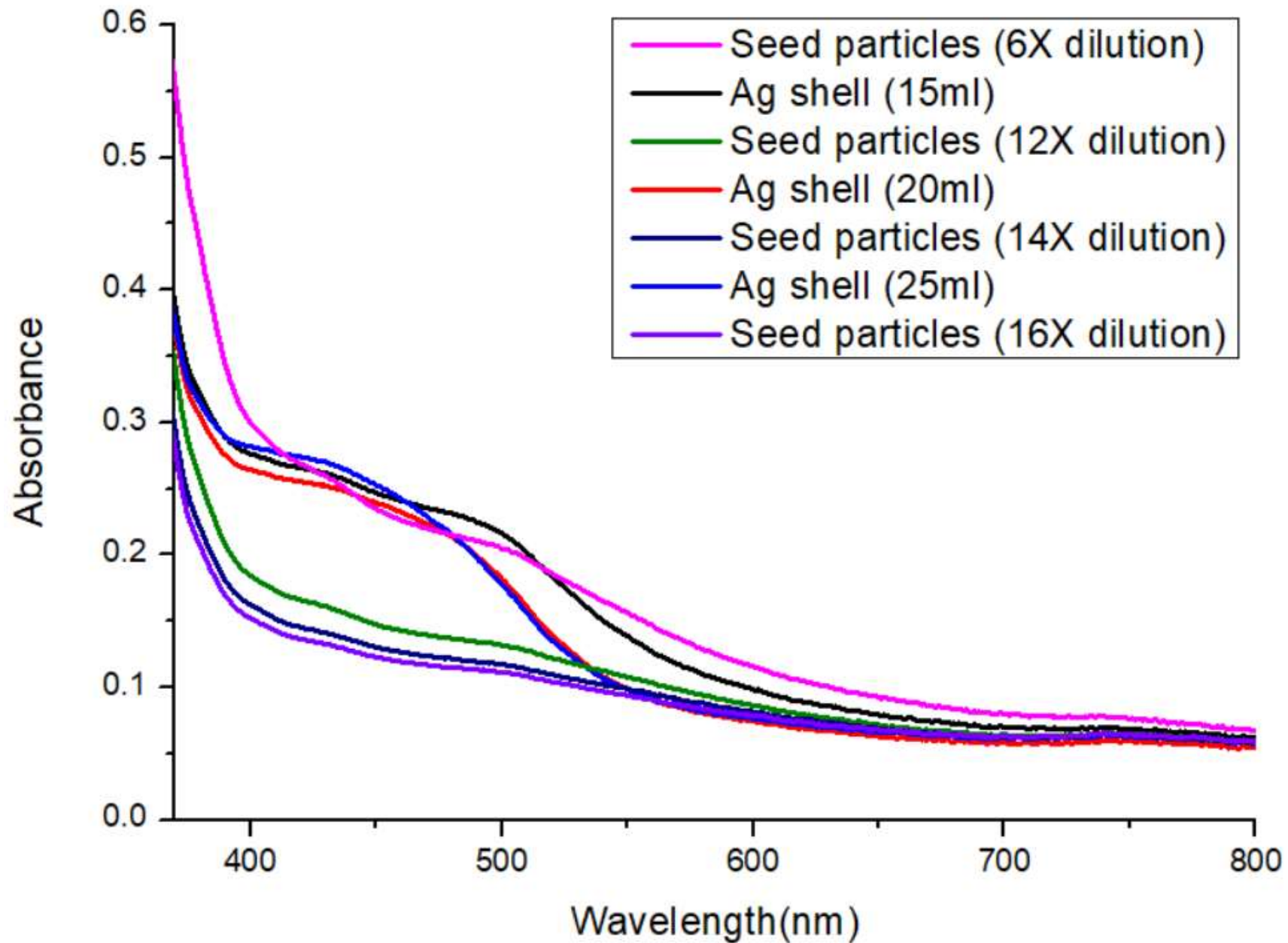
- **GNP Sample** : 2.5ml made up to 15 ml (core solution) (TA 0.15mM)
- **Silver Nitrate solution** : 0.06 mM (shell solution)
- Solutions are prepared with DI water.
- 15 ml of GNP sample is taken in 2 beakers, silver salt solution is added

Impeller Rotation – 1000 rpm | Silver Nitrate : 0.06 mM

Input flow rate : 1 ml / min | No. of drops / ml : 20 - 25

Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	15	7
2	Dropwise	10	15	0.06	20	7
3	Dropwise	10	15	0.06	25	7





Experiment 4 : Core – Shell Particles - II

(Ag core, Au Shell) Trial 2

- **SNP Samples** : 2.5 ml made up to 15 ml (core solution) (TA 0.3mM)
- **Chloroauric acid solution** : 0.06 mM | 0.12mM (shell solution)
- Solutions are prepared with DI water.
- pH is adjusted using 10 w/v of Potassium Carbonate solution
- 15 ml of SNP sample is taken in each beaker, gold salt solution is added

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 0.12 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	60	6 – 7
2	Dropwise	10	15	0.06	40	6 – 7
3	Dropwise	10	15	0.12	25	7
4	Dumped	10	15	0.12	21	7

