Synthesis of Metal Colloids

Caution: *Since the colloid synthesis is sensitive to various laboratory conditions and the practices of the individual researchers, the following procedure should be taken as a general guideline. One may have to vary the experimental conditions to suit their needs.*

Preparation of 2.5 x 10^{-4} M Gold Colloids (Sodium Citrate Reduction Method)

1. Make a solution of ~5.0 x 10^{-3}M $HAuCl_4$ in water. (0.1699 g $HAuCl_4$ in 100 mL deionized H_2O)
2. Take 1 mL of that solution and add it to another 18 mL of H_2O.
3. Make a solution of 0.5% sodium citrate (0.25g in 50 mL of H_2O).
4. Heat the 19 mL solution of $HAuCl_4$ until it begins to boil.
5. Add 1 mL of 0.5% sodium citrate solution, as soon as boiling commences.
6. Continue heating until colour change is evident (pale purple).
7. Remove the solution from the heating element and continue to stir until it has cooled to room temperature.
8. Top the solution up to 20 mL to account for boiling.

This is an old method (refereed as Turkevich method) which yields fairly uniform size colloids with diameter of 15-20 nm. See reference Turkevich, J.;Stevenson, P. L.;Hillier, J.Discuss. Faraday Soc. 1951, 11, 55

Preparation of Gold Particles in Toluene:

A. Hydrogen tetrachloroaurate (30 mL of 30 mM, in water).

Mass = 393g/mol □ 0.03 M □ 30mL/1000mL

= 0.3537g of $HAuCl_4$ in 30mL of H_2O

B. Tetraoctyl ammonium bromide (80 mL in 50 mM, in toluene).

Mass = 546.8g/mol □ 0.05 M □ 80ml/1000mL

= 2.187g of TOAB in 80mL of toluene

1. Prepare 2.19 g of tetraoctyl ammonium bromide in 80 mL of toluene.

2. Add solution prepared in step 1. to a solution of hydrogen tetrachloroaurate (0.3537 g in 30 mL of H_2O).
3. Stir for 10 min.
4. Vigorously stir reaction mixture and add $NaBH_4$ (0.38 g in 25 mL of H_2O) dropwise over a period of ~30 min. (Ensure that organic and aqueous phases are being mixed together).
5. Stir solution for an additional 20 min.
6. Extract organic phase and wash once with diluted H_2SO_4 (for neutralization) and five times with distilled water.
7. Dry organic layer with Na_2SO_4.

For platinum particles substitute dihydrogen hexachloroplatinate (IV) ($PtCl_6$ H_2O) for $HAuCl_4$ and for iridium particles substitute H_2IrCl_6 $4H_2O$ for $HAuCl_4$.

> Yields highly concentrated gold colloidal suspension with particle diameter in the range of 5-10 nm. Can be suspended in both polar and nonpolar solvents.

Adopted from the reference Brust, M.;Walker, M.; Bethell, D.;Schffrin, D. J. Whyman, R., *J. Chem. Soc., Chem. Commun.*, 1994, 801-802 and George Thomas, K.Kamat, P. V. *J. Am. Chem. Soc.* 2000, *122*, 2655

Preparation of 1.0 x 10^{-3}M Ag Colloids (Sodium Citrate Reduction Method)

1. Make a solution of ~ 5.0 x 10^{-3}M $AgNO_3$ in water. (0.0425 g in 50 mL deionized H_2O).
2. Take 25 mL of that solution and add it to another 100 mL of H_2O (now ~1.0 x 10^{-3}M).
3. Make a solution of 1% sodium citrate (0.5 g in 50 mL of H_2O).
4. Heat the 125 mL solution of $AgNO_3$ until it begins to boil.
5. Add 5 mL of 1% sodium citrate solution, as soon as boiling commences.
6. Continue heating until a colour change is evident (pale yellow).
7. Remove the solution from the heating element and continue to stir until it has cooled to room temperature.
8. Top the solution up to 125 mL to account for boiling.

This method yields relatively large size silver nanocrystallites with a diameter of 60-80 nm and exhibits abs. max. ~420 nm. See reference:

J. Phys. Chem. B, 1998, *102*, 3123

(Note: Use of Sodium Borohydride as a reductant can give smaller size silver nanoparticles with plasmon absorption around 380 nm. Presence of citric acid or polyvinyl alcohol can provide additional stability to these colloids)

Preparation of Au Capped Ag

1. Take 125 mL of 1.0 x 10^{-3}M solution of Ag colloids and add 12,5 mL H_2O.
2. Heat this solution until it comes to a boil and then add the appropriate amount of 5.0 x 10-3M $HAuCl_4$. (For example: 50 L, 100 L, 150 L, 300 L, and 500 L)

Silver Nanocrystal Preparation in Organic Medium (Using TOAB)

Modification of method found in source: Korgel, B.A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. *J. Phys. Chem. B* **1998**, *102*, 8379-8388. (The method described in this paper yields a precipitate of AgBr in the initial extraction process)

1. Prepare ~5.0M $NaNO_3$ in deionized water (12.749g $NaNO_3$ in 30mL H_2O).
2. Prepare ~50mM TOAB in toluene (1.367g tetraoctylammonium bromide in 50mL toluene).
3. Add the TOAB/toluene solution to the $NaNO_3$/water solution.
4. Stir vigorously for 1 hour (to remove Br^- ions from solution and prevent the formation of AgBr when $AgNO_3$ is added).
5. Extract organic phase and set aside. Discard aqueous phase.
6. Prepare ~30mM $AgNO_3$ in water (0.0764g $NaNO_3$ in 14mL H_2O).
7. Add 7.5mL of 30mM $AgNO_3$ solution to the organic solution.
8. Stir vigorously for 45 minutes.
9. Extract organic phase (discard aqueous layer).
10. Add 0.16mg (~0.189mL) of 1-dodecanethiol to organic solution (to cap the silver)
11. Stir vigorously for 15 minutes.
12. Meanwhile, prepare ~0.4M $NaBH_4$ in water (0.3783g $NaBH_4$ in 24mL H_2O).
13. Add 6.25mL of the $NaBH_4$,dropwise over a 35min. period, to the solution containing the silver (organic layer), while stirring vigorously.
14. Stir for ~15 hours (overnight).
15. Extract organic layer (discard aqueous layer).
16. Wash organic layer 3 times with dilute ethanol.
17. Allow to settle, and extract organic layer.
18. Store is closed container.