Hong Kong Chemistry Olympiad for Secondary Schools (2009-2010)

Theme of Year: Chemistry of Metal

Theme metal: Silver

Project title: How to produce Silver nanoparticles in a efficient way

School name: The Church of Christ in China Heep Woh College

Student Name: (1) To Hing Lui(English) (Chinese)

(2) Lim Kam Ho(English) (Chinese)

(3) Chun Hon Sun(English) (Chinese)

(4) Yu Kin Ching(English) (Chinese)

(5) Yip Tsz Fung (English) (Chinese)

Report

Project title: How to produce Silver nanoparticles in a efficient way

Objective:

Making silver nanoparticles by an effective method and can be produced with a large amount. The silver nanoparticles can be reduced by sodium citrate and stabilized by PVA solution.

Abstract:

Silver nanoparticles are silver particles with no larger than 100nm size, through redox reaction between $AgNO_3$ and sodium citrate, silver nanoparticles are the products. $AgNO_3$ can be reduced by sodium citrate and stabilized by PVA solution. But the reaction affected by the content of PVA, citrate and the time for heating and stirring. As a result, doing 4 different experiments is needed, it can be test the most suitable content of PVA, citrate and time for heating and stirring to the silver nitrate mixture to make a success silver nanoparticles solution.

Principle:

As we are chemically making silver nanoparticles which are silver particles in nanometer size, they can be used to killing bacteria since the silver nanoparticles can combine with the cell wall or membrane of pathogenic bacteria, the particles can directly and quickly combine with the oxygen metabolism enzyme thiol (-SH), so that enzyme is inactive, and block their respiratory.

To make silver nanoparticles, a numbers of experiments have to be carried out. The final product of the set of the experiment is a clear solution in yellow colour, as the silver nanoparticles which are yellow in colour are separated and further be stabilized in order to prevent the silver nanoparticles to aggregate with each other to form silver which is a black insoluble power.

Silver nitrate is a white solid and it can be used to make silver nanoparticles as it is least expensive salt of silver; it offers several other advantages as well. It is non-hygroscopic, in contrast to silver fluoroborate and silver perchlorate. It is relatively stable to light. Finally, it dissolves in numerous solvents, including water. We mix it together with trisodium citrate and keep on stirring and heating it to let reaction to take place.

Sodium borohydride is an inorganic compound with the formula $NaBH_4$. This white solid, usually encountered as a powder, it is a reducing agent that can be used to reduce silver nitrate, however it is poisonous and flammable, which will raise a hazard while using.

Trisodium citrate has the chemical formula of $Na_3C_6H_5O_7$. It is sometimes referred to simply as sodium citrate, it is a white crystalline powder, which is a reducing agent we will use in the experiments, it is non-poisonous, so it is safe to use, and it is soluble in water, it is suitable for us to

use as the main solvent of our solutions is water.

From a former study of making silver nanoparticles, the former study makes use of sodium borohydride and silver nitrate to make silver nanoparticles. However, as borohydride is poisonous, citrate, which is non-poisonous, will be used instead of borohydride. A redox reaction is expected to occur. The equation is shown as below

$2Ag^{+} + C_6H_5O_7^{3-} \rightarrow 2Ag + C_5H_4O_5^{2-} + CO_2 + 2H^{+}$

Polyvinyl alcohol is a polymer that has excellent film forming, emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. PVA can be used as the stabilizer since it is water-soluble and large in molecular size which means it is able to block the aggregation of silver nanoparticles. It is also safe while using, however it requires a longer time for the reaction to complete.

Chemical use:

Silver Nitrate	$AgNO_3$
Sodium Citrate	$C_6H_5O_7Na_3$
Sodium Borohydride	$NaBH_4$
Polyvinyl alcohol (PVA)	$(CH_2CHOH)_n$

Chemical Hazards:

Silver nitrate is corrosive, causing burns in contact with the skin and eyes.
Sodium borohydride is flammable and toxic.
Sodium citrate and PVA are irritants; avoid contact with skin and eye, ingestion and inhalation. Labeled waste containers should be made available for any waste colloidal silver and unused borohydride solution (which must be freshly made every day).

Apparatus and Materials used

Flat-bottomed flasks, glass rods, measuring cylinders, reagent bottles, beakers, pipettes, heater and stirrer, electric balance and droppers.

Experimental method:

Four sets of experiments have been done.

Part 1: To determine the most suitable concentration for Sodium Citrate

For the part 1, it was aimed as to find the best proportion of Sodium Citrate.

The following procedures have been followed:

1. Mix 30mL 0.05mM Silver Nitrate with different proportions of 1% Sodium Citrate and distilled water shown below. The concentration of sodium citrate employed for the reduction was kept low to avoid the presence of excess citric acid in the silver suspension.

Set	Silver nitrate/mL	Sodium citrate/mL	Distilled water/mL	Total volume of the solution/mL
1	30	20	0	50
2	30	10	10	50
3	30	4	16	50
4	30	2	18	50

2. Heat and stir each set up for the same time
3. A timer was used during heating and stirring to count the time.
4. Observe the solutions after heating and stirring.

Part 2: To determine the most suitable concentration for PVA

For the part 2, it was aimed as to find out the most suitable content of PVA for the silver nitrate mixture to make Silver Nanoparticles as PVA can be used to prevent the decomposition of citrate.

The following procedures have been followed:

1. Mix 10mL 0.05mM Silver Nitrate with different volumes of NaBH4, PVA and distilled water shown below.

Set	NaBH4/mL	Silver Nitrate/mL	PVA/mL	Distilled water/mL
1	30	10	5	5
2	30	10	No	10
3	30	10	10	No

2. Heat and stir each set up for the same time
3. A timer is used during heating and stirring to count the time.
4. Observe the solutions after heating and stirring.

Part 3: To determine the most suitable concentration for making Silver Nanoparticles

For the part 3, it was aimed as to find out the suitable amount of PVA and sodium citrate to be used, in order to achieve a better result of Silver nanoparticles product.

The following procedures have been followed:

1. Mix 0.05mL Silver Nitrate with PVA, 1%Sodium Citrate and distilled water as shown below.

Silver Nitrate/mL	PVA/mL	Sodium citrate/mL	Distilled water/mL	Time/minute
30ml	10ml	10ml	No	40
20ml	10ml	10ml	10ml	40
20ml	20ml	10ml	No	40
20ml	10ml	20ml	No	40

2. Heat and stir each set up for the same time
3. A timer was used during heating and stirring to count the time.
4. Observe the solutions after heating and stirring.

Part 4: To determine the most suitable time for making Silver Nanoparticles

For the last experiment, it was aimed as to find out the most suitable time for heating and stirring the best Silver Nitrate mixture in the above experiments so the Silver nanoparticles could be made perfectly.

The following procedures have been followed:

1. Mix 20mL 0.05mM Silver Nitrate with 10mL PVA and 20mL Sodium Citrate

Set	Silver nitrate/mL	Sodium citrate/mL	PVA/mL	Time/min
1	20	20	10	20
2	20	20	10	30
3	20	20	10	40
4	20	20	10	50

2. Heat and stir each set up for different time as shown below
3. A timer was used during heating and stirring to count the time.
4. Observe the solutions after heating and stirring

Result:

Part 1: To determine the most suitable concentration for Sodium Citrate

Set 1: A very pale yellow solution was obtained.

Set 2: A very clear solution in yellow colour wasobtained.

Set 3: A cloudy solution in dark yellow colour was obtained and black precipitates were found.

Set 4: A very cloudy solution in very dark yellow colour was obtained and many black precipitates were found

Overall interpretation

When the citrate concentration was low, there was excess silver nanoparticles, and they aggregated to become the black silver particles which were in bigger size. There were not enough citrate ions to stabilize the silver nanoparticles.

When the citrate concentration was too high, there is excess citrate, which was colorless in aqueous form and they can fade the color of the solution

The set 2 was the most favorable portion for the citrate can work to separate the silver nanoparticles of 10 mL as a very clear solution in yellow colour was obtained.

Silver Nanoparticle was prepared. (Success)

Silver Nanoparticle was not prepared.(Failed)

Part 2: To determine the most suitable concentration for PVA

Set 1: It had some black precipitates.

Set 2: The silver nanoparticles tended to become silver precipitates.

Set 3: The resulting solution was clear and had nearing no silver precipitates.

Overall interpretation

When there was not enough PVA, the silver nanoparticles tended to become silver precipitates.

When there was too many PVA, the solution should take much longer time to react.

The set 3 was the most suitable content of PVA for the silver nitrate mixture to make silver nanoparticles of 10mL as the resulting solution was clear and had nearing no silver precipitates.

Part 3: To determine the most suitable concentration for making Silver Nanoparticles

Set 1: In this set of experiment, there were some precipitates which can reflect light. It was calmed that those are silver particle.

Set 2: The solution became dark yellow as there were silver precipitates.

Set 3: The solution had been boiling for about 40min but had no visible observation.

Set 4: After heating the solution for about 20min, the solution started to turn from colorless to pale yellow. About 25-30min, it was still at a yellow color. From the 30-37 min, the solution started to turn form pale yellow to a bit greenish.

Overall interpretation

Since sodium citrate was used to separate silver particle, if there was not enough sodium citrate supplied, silver particle would aggregate and form a particle large in size.

In addition, too much PVA would slow down the reaction greatly

The Set 4 was the most suitable proportion to make silver nanoparticles which the ratio of PVA, sodium citrate and silver nitrate was 1:2:2 as the silver particles in the solution were the least except set 3. It is because there was a reaction in set 1, 2 and 4 in 40minutes, but no reaction in set 3.

Part 4: To determine the most suitable time for making Silver Nanoparticles

Set 1: The solution turned very pale yellow.

Set 2: The solution turned yellow with a little bit precipitate, but it was yellow with no precipitates when it was boiled for about 25 minutes.

Set 3: The solution turned dark yellow.

Set 4: The solution turned dark yellow.

Overall interpretation

When the time for heating and stirring was too long and the citrate decomposes, the silver nanoparticles aggregated and formed silver precipitate and turn the yellow dark.

When the time for heating and stirring was not enough, it would not produce silver nanoparticles.

25 minutes are the most suitable time for heating and stirring the silver nitrate mixture to make silver nanoparticles.

Discussion:

In that experiment, there are the following possible improvements or importance should be reminded.

1. **The source of water**

   In that experiment, it was essential to use distilled water in dilution of chemical. Therefore, tap water would not be suitable to be used. Tap water contain chloride ion which would form compound with the silver particle in the Silver nitrate solution and form precipitate. This for sure affect the result obtained. In order to get pure H2O compound, distilled should be used instead of tap water.

2. **Better temperature control**

   In the experiment, the solution was to be boiled to ensure the reaction take place. However, if there was too much energy supplied, is would faster the reaction and the silver nanoparticles may aggregate. A silvery precipitate would form in the bottom of the flask. That was not a good result.

Other then the improvement of the producing process, it's also useful to further investigate the silver nanoparticles.

1. TEM (Transmission electron microscopy)

   It can try to find out how the silver nanoparticles look likes and see how big actually it is by using transmission electron microscopy. This helps us understand more about the particle. And then it can be compare the particles of the silver nanoparticles product with the nanoparticles we prepared.

2. Find out more uses of silver nanoparticles

   Silver nanoparticles are not commonly used nowadays. However, if the Silver nanoparticles can be controlled stably, it could widely used in killing bacteria. This must greatly improve our living standard.

Conclusion:

In the four parts of experiments, we have compared those experiments results and differentiated which one is the best.

According to those experiments result, in part 1, the set 2 was the most favorable portion for the citrate can work to separate the silver nanoparticles of 10 mL because a very clear solution in yellow colour obtained in set 2.

In part 2, the set 3 was the most suitable content of PVA for the silver nitrate mixture to make silver nanoparticles of 10mL because the resulting solution was clear and has nearing no silver precipitates.

In experiment 3, the set 4 was the most suitable proportion to make silver nanoparticles as the silver particles in the solution are the least. The ratio of PVA, sodium citrate and silver nitrate was 1:2:2.

In experiment 4, 25minutes are the most suitable time for heating and stirring the silver nitrate mixture to make silver nanoparticles.

As the result, the best method to produce silver nanoparticles was obtained.

References

1. *Alain Roucoux, Jürgen Schulz, and Henri Patin Chem. Rev. 2002, 102, 3757-3778*
2. *Sally D. Solomon; Mozghan Bahadory; Aravindan V. Jeyarajasingam; Susan A. Rutkowsky; Charles Boritz J. Chem. Educ. 2007, 84, 322-325*
3. *Lee, P. C.; Meisel, D. J. Phys. Chem. 1982, 86, 3391–3395.*
4. *Kamat, P. V.; Flumiani, M.; Hartland, G.V. J. Phys. Chem. B 1998, 102, 3123–3128.*