Green synthesis of silver nanoparticles and silver colloidal solutions

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Abstract. In this paper, silver colloidal solutions have been synthesized rapidly in green conditions by using microwave irradiation and non-toxic chemistry substances (acid oxalic, silver nitrate, polyvinyl pyrrolidone (PVP; Mw = 55 000)). The particle size and morphology of these solutions can be controlled by altering several factors like the time, the power of microwave exposure, and the ratio of silver oxalate and PVP etc. The silver nanoparticles were fabricated by thermal decomposition of silver oxalate. The synthesized silver colloidal solutions and silver nanoparticles were characterized by several analytical techniques like UV–VIS, XRD, TEM, FESEM/EDS and ICP-AAS studies. Finally, we used the synthesized silver colloidal solutions for antibacterial purpose. The obtained results showed that the synthesized silver colloidal solutions, even at very low concentrations, have highly efficient anti-bacterial property.

Keywords: Silver nanoparticles, silver colloidal solutions, green synthesis.

1. Introduction
Silver nanoparticles have potential applications in various fields such as the environment, biomedicine, catalyst, optics and electronics [1-4]. Silver nanoparticles have also drawn much attention because they show high bactericidal effects [5-9]. Various approaches to synthesis metal nanoparticles have been reported such as chemical reduction, UV photolysis, gamma irradiation, metal vapor deposition, laser ablation, sputtering... Among these, chemical reduction has been the most extensively investigated [1, 2]. In this paper, thermal decomposition of silver oxalate complexes to fabricate high purity silver nanoparticles and reduction of silver oxalate complexes by ethyleneglycol using polyvinyl pyrrolidone as the capping agent has been explored. These reactions have been assisted by microwave irradiation because of other conventional heating methods. The main advantages include (i) the initial heating process is rapid, (ii) uniform heat transfer to the solution and (iii) microwave induces the generation of localized high temperatures at reaction sites, which enhances the reaction rate [1, 2].
2. Experimental

2.1. Preparation of silver oxalate precursor
Silver oxalate was prepared by mixing 50 ml of 0.5 M AgNO\textsubscript{3} (Merck, 99%) solution with 30 ml of 0.5 M oxalic acid (Merck, 99%). The white formed precipitate was filtered, washed with distilled water, dried in an air oven for 1 h and stored in a dark bottle [1, 2].

Fabrication of silver nanoparticles: Silver nanoparticles were produced by thermal decomposition of silver oxalate.

Fabrication of silver colloidal solutions: 40 ml of ethylene glycol (China, 99%), 0.25 g of polyvinyl pyrrolidone (PVP, Mw \approx 55 000, BASF-Germany, 99%) was added and stirred. Then, the complete dissolution of PVP, Ag\textsubscript{2}C\textsubscript{2}O\textsubscript{4} was added, stirred for 10 mins and purged with N\textsubscript{2} gas for 10 mins. Immediately, the reaction vessel was irradiated in microwave cavity for different time intervals. All the reactions were carried out in a microwave oven operating in a cycling mode (on for 1 minute, off for 1 minute) to prevent the intense boiling of solvents as well as the agglomeration of metals.

2.2. Characterization
The synthesized silver colloidal solutions and silver nanoparticles were characterized by advanced analytical techniques such as UV–VIS (Cary 100 Conc, Varian), XRD (D8 Advance, Bruker - Germany), TEM (JEM-1400, Japan), FE-SEM/EDS (JSM 7401F, Japan) and ICP-AAS studies. Antibacterial (E. Coli) efficiency of silver colloidal solutions was determined by Colony Count Test Method.

3. Results and discussion

3.1. Preparation and characterization of silver oxalate
Silver oxalate was prepared with high yield and was confirmed by powder XRD (figure 1). The interplanar d-spacings of the corresponding lines presented in the powder XRD pattern match those of standard sample, which corresponds to the primitive monoclinic system. Moreover, it is clear from XRD that no other phase of silver oxalate is presented in the as-synthesized silver oxalate. The FE-SEM image of silver oxalate shows particles in the size range of under 2\,\textmu m (figure 2) The EDS results of silver oxalate showed that the weight percent of atoms (Ag = 71.22%; C = 8.54%; O = 20.24%), which agrees with the theoretical calculations from formula of Ag\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (Ag = 71.05%; C = 7.9%; O = 21.05%) (figure 3).

Figure 1. XRD pattern of silver oxalate.
3.2. Synthesis of silver nanoparticles

A method for fabrication of highly pure silver nanoparticles without requiring the addition the capping or reducing agents is thermal decomposition of silver oxalates. This high pure silver can be used in the field of electronics requiring high conductivity or in the field of bacteria resistance requiring high purity [1-4].

The XRD pattern of the M1 sample (calcinated at 140°C in 1 h) (figure 4) showed that when calcinating at 140°C in 1 h, silver oxalate was decomposed partially to generate silver (the red peak), the main remaining were also silver oxalates (the blue peak). Thus, we decided to increase the temperature of calcination to 200°C in 1 h and it is interesting that silver oxalate was completely decomposition to generation silver nanoparticles. The XRD powder pattern of the Ag is given in figure 5. Interplanar distance \(d\) corresponding to facets (111), (200), (220), (311) and (222) is \(d=2.35568\) (2θ=38°); 2.04057 (2θ=44°); 1.44352 (2θ=64°); 1.23130 (2θ=77°); 1.17926 (2θ=82°), respectively. These data match Ag standard sample. The crystalline size of Ag nanoparticles was calculated from Sherrer formula is 70 nm.
3.3. Synthesis of silver colloidal solutions

The Ag colloids were synthesized by altering several factors such as concentration of silver nitrate, exposure time and power of microwave. The results were presented in table 1.

(a) UV-VIS results

The results from UV-VIS of the samples are illustrated in figures 6, 7, 8, 9, and 10. Figure 6 shows the UV-VIS absorbance spectra of the solutions in groups 1a, 1b, 1c, 1d and 1e. These samples are made at high concentration of silver nitrate. The peak intensity increases as the samples are treated in microwave for longer time and it is seen that the position of the peaks are red shifted (from 405 to 410, 411, 416, 420 nm) corresponding with the increasing of MW exposure time (from 4 min to 4 min 10 sec, 4 min 20 sec, 4 min 30 sec). Thus, with the same of concentration of AgNO$_3$, power of MW irradiation, when increasing time of MW exposure, the size of nanoparticles is larger via UV-Vis results.

Figure 7 shows the UV-VIS absorbance spectra of the solutions in groups 2a, 2b, 2c, 2d and 2e. These samples are made at low concentration of silver oxalate. The peak intensity increases as the samples are treated in microwave for longer time and it is seen that the position of the peaks are red shifted (from 405 to 410, 411, 416, 420 nm) corresponding with the increasing of MW exposure time (from 4 min to 4 min 10 sec, 4 min 20 sec, 4 min 30 sec).

Table 1. Silver colloidal solutions.

| Samples | Ethylene glycol(ml) | PVP(g) | Ag$_2$C$_2$O$_4$(g) | Ag$_2$C$_2$O$_4$:PVP | Power(W) | Time     |
|---------|---------------------|--------|---------------------|---------------------|----------|----------|
| 1a      | 40                  | 0.25   | 0.05                | 1:5                 | 160      | 4 min    |
| 1b      | 40                  | 0.25   | 0.05                | 1:5                 | 160      | 4 min 10 sec |
| 1c      | 40                  | 0.25   | 0.05                | 1:5                 | 160      | 4 min 20 sec |
| 1d      | 40                  | 0.25   | 0.05                | 1:5                 | 160      | 4 min 30 sec |
| 1e      | 40                  | 0.25   | 0.05                | 1:5                 | 160      | 4 min 40 sec |
| 2a      | 40                  | 0.25   | 0.025               | 1:10                | 160      | 4 min    |
| 2b      | 40                  | 0.25   | 0.025               | 1:10                | 160      | 4 min 10 sec |
| 2c      | 40                  | 0.25   | 0.025               | 1:10                | 160      | 4 min 20 sec |
| 2d      | 40                  | 0.25   | 0.025               | 1:10                | 160      | 4 min 30 sec |
| 2e      | 40                  | 0.25   | 0.025               | 1:10                | 160      | 4 min 40 sec |
| 3a      | 40                  | 0.25   | 0.01                | 1:25                | 160      | 4 min    |
| 3b      | 40                  | 0.25   | 0.01                | 1:25                | 160      | 4 min 10 sec |
| 3c      | 40                  | 0.25   | 0.01                | 1:25                | 160      | 4 min 20 sec |
| 3d      | 40                  | 0.25   | 0.01                | 1:25                | 160      | 4 min 30 sec |
| 3e      | 40                  | 0.25   | 0.01                | 1:25                | 160      | 4 min 40 sec |
| 4a      | 40                  | 0.25   | 0.025               | 1:10                | 800      | 30 sec   |
| 4b      | 40                  | 0.25   | 0.025               | 1:10                | 800      | 35 sec   |
| 4c      | 40                  | 0.25   | 0.025               | 1:10                | 800      | 40 sec   |
| 5a      | 40                  | 0.25   | 0.01                | 1:25                | 800      | 40 sec   |
| 5b      | 40                  | 0.25   | 0.01                | 1:25                | 800      | 50 sec   |
shifted (from 404 to 405, 412, 414, 415nm) corresponding with the increasing of MW exposure time (from 4min to 4min 10s, 4min 20s, 4min 30s). However, the peak position changed very slightly.

Figure 5. XRD pattern of M2 (200°C in 1 hour).

Figure 6. UV-VIS Absorbance spectra of the solutions in groups 1 shows the peak (nm): 1a (405); 1b (410); 1c (411); 1d (416); 1e (420).

Figure 7. UV-VIS absorbance spectra of the solutions in groups 2 shows the peak (nm): 2a (404); 2b (405); 2c (412); 2d (414); 2e (415).

Figure 8. UV-VIS absorbance spectra of the solutions in groups 3 shows the peak (nm): 3a (410); 3b (409); 3c (409); 3d (410); 3e (409).

Figure 9. UV-VIS absorbance spectra of the solutions in groups 4 shows the peak (nm): 4a (402); 4b (411); 4c (420).
Figure 8 shows the UV-VIS absorbance spectra of the solutions in groups 3a, 3b, 3c, 3d and 3e. These samples are made at very low concentration of silver oxalate. There is no significant difference on the absorption peak positions at different times of exposure.

Figures 9 and 10 show the UV-VIS absorbance spectra of the solutions in groups 4a, 4b, 5a, 5b. These samples are made at high power of MW. This indicated that the higher the power is, the shorter the time is.

![Figure 10. UV-VIS absorbance spectra of the solutions in groups 5 shows the peak (nm): 5a (407); 5b (411).](image)

(b) Characterized by TEM

The TEM image of the 3c sample showed that the average size of silver nanoparticles is about 20nm.

![Figure 11. TEM of 3c sample.](image)

(c) Microbiological test

Antibacterial effects of the Ag nanoparticles were studied using Colony Count Test Method. The effect of E. Coli (Gram-negative) bacterial strains is determined by the relation

\[
\mathcal{d} = \frac{N_1 - N_2}{N_1} \times 100\%
\]

where \(\mathcal{d}\) is the percentage of bacterial reduction, \(N_1\) is the number of surviving bacterial colonies from the control sample, and \(N_2\) is the number of surviving colonies from test samples.

All the samples (2c, 2d, 2e, 3c, 3d, 3e) have been diluted 1:12 before testing. The results of E. Coli antibacterial property of Ag solutions are shown in figure 12. No bacterium was detected in all the diluted samples (2C, 2D, 2E, 3C, 3D, 3E) after 5 minutes, the antibacteria efficiency is \(\mathcal{d} = 100\%\).

(d) ICP-AAS results

ICP-AAS results on 3D and 2D solution showed silver nanoparticles content in 3D solution is 17.8mg/l (i.e. concentration of Ag in 3D solution is 17.8 ppm) and in 2D is 12.7mg/l (concentration of Ag in 3D solution is 12.7 ppm). Thus, E.coli was killed completely at very low concentration (12.7 ppm). From ICP-AAS results, we calculated the yield of reactions (2D solution: 48.11% and 3D solution: 85.81%).

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\[d_0 = 18.87 \pm 2.083\text{nm}\]
4. Conclusions
- Fabricated successfully silver oxalate with high yield. The average particle sizes are under 2 µm. The results of XRD and FESEM with EDS showed as-fabricated silver oxalate are highly pure.
- The thermal decomposition of silver oxalate at 200°C to receive silver particles. The results of XRD demonstrated these silver particles have high purity with the average size is about 70 nm.
- Silver colloidal solutions have been synthesized rapidly in chemical green condition. The UV-VIS spectra showed that these as-synthesis samples have absorbance peak from 402 to 420 nm. The average size of silver nanoparticles is about 20 nm via TEM images. The yields of reactions are from 48.11% to 85.81%. These colloidal solutions have highly efficient anti-E. Coli property at very low concentration (12.7 ppm). Our further research is finding suitable conditions to increase the yield of reaction and to decrease the size of silver nanoparticles.

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