PREPARATION OF CHITOSAN-STABILIZED SILVER (Chi-Ag) NANOPARTICLES USING DIFFERENT REDUCING AGENTS AND TECHNIQUES

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ABSTRACT

Metal with nanoparticles size and dispersed particles is part of nanotechnology development including computer nanochips, medicals, ceramics, catalysts etc. Nano and dispersed particles of silver have been synthesized in this study, by reducing the silver ions in chitosan solution. The silver ions were reduced by refluxing in methanol, using sodium borohydride and hydrazine as reducing agent or photo-irradiation technique to produce silver nanoparticles. Silver metal particles were characterized with UV-Vis Spectroscopy and TEM (Transmission Electron Microscopy). TEM data shows that silver particles were aggregated and in size of >10 nm if hydrazine was used as the reducing agent. Silver nanoparticles prepared by refluxing in methanol were less aggregated as particle size of > 10 nm with relative deviation of $\sigma/d = 0.2$. Dispersed silver particles with size of 3.2-12.6 nm were fabricated by using sodium borohydride as the reducing agent or photo-irradiation as the reducing technique. With these techniques, silver particles were dispersed and nearly in uniform size compared with methanol and hydrazine technique. Sodium borohydride reduced silver ions much faster than other techniques.

Keywords: silver nanoparticles, chitosan, nanotechnology

1. INTRODUCTION

The potential applications of nanotechnology have brought about revolution in computing, electronic, materials design, medicine, energy, catalysis and numerous other fields. Attempts to obtain metal particles including silver in nanometer-size, dispersed with narrow particle-size-distribution have been research interest recently since they have important roles in development of nanotechnology. There have been several methods for the preparation of silver nanoparticles that have been reported. The methods include chemical reduction of silver without stabilizer, thermal evaporation as silver aerosol or reduction of silver in fatty acid film. Silver sol preparations by chemical and photo-reduction in reverse micelle have also been published. The photophysical preparation was developed by others. Silver colloidal nanoparticles have been prepared with various synthetic polymers. However, silver colloidal nanoparticles stabilized by chitosan reduced by various methods or technique remains unexplored.

2. MATERIALS AND METHODS

2.1 Chemicals

The following commercially available materials were used without further purification. Chitosan of medium molecular weight ~400000 (< 10% chitin) (Fluka, Switzerland). Hydrazine (99%) and acetic acid glacial (99.8%) (both BDH, England). Sodium borohydride 95% (Riedel-de Haen, Germany). Silver nitrate (99.8%) (Johnson Matthey, England).

2.2 Instrumentation

A transmission electron microscopy (TEM) Model: Philip CM 12 was used for determination of metal particle size and the particle dispersion. A UV-Vis spectrophotometer model: Hitachi U2000 & Jasco V-530 was used to record silver plasmon band and an atomic absorption spectrophotometer (AAS) model: Perkin Elmer 3100 (acetylene) was used for determination of silver content. The sample preparations for all these analyses were followed the reported procedure. The chitosan-metal colloids were digested prior to AAS analyses. Samples were labeled as Chi-Ag-me, Chi-Ag-nb and Chi-Ag-hz for preparation using methanol, sodium borohydride and hydrazine as the reducing agents. Chi-Ag-ir is a sample notation for chitosan-stabilized silver colloid using photo-irradiation as the reducing technique.

2.3 Chitosan-silver Colloids

The chitosan-stabilized silver metal colloids (Chi-Ag) were prepared by modified reported procedure as follows. Silver stock solution was prepared in concentration of $10^{-4}$ mol/ml from silver nitrate.
Another set of experiments were prepared by dissolving 5.6 x 10^{-2} mol (0.0900 g) of chitosan in 88.8 ml of 1.5% aqueous acetic acid solution and diluted with addition of 90 ml of methanol with vigorous stirring. Then, 1.12 ml (1.12 x 10^{-4} mol) of silver stock solution was very slowly added to the above solution (total volume became 180 ml) and kept stirring for 1 h. The volume of the acetic acid solution in each chitosan-Ag solution might have slightly varies depending on the volume of sodium borohydride or hydrazine added but generally the volume of 1.5% acetic acid added was not less 40% of the total volume solution except in experiments studying the effect of water content. The silver ions were reduced either by reflux, addition of sodium borohydride, hydrazine or photo-irradiation with a 100 Watt tungsten lamp. After the Chi-Ag was prepared the total volume was measured again to maintain at constant volume. A few drops of methanol were added if the total volume decreased during the preparation.

Table 1. Composition of Chi-Ag solution for studies of water content effect

<table>
<thead>
<tr>
<th>Water content/%v/v</th>
<th>Aqueous HOAc</th>
<th>MeOH/ml</th>
<th>Ag stock solution/ml</th>
<th>Total volume/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>16.9</td>
<td>1.263</td>
<td>162</td>
<td>180</td>
</tr>
<tr>
<td>20</td>
<td>34.9</td>
<td>0.621</td>
<td>144</td>
<td>180</td>
</tr>
<tr>
<td>30</td>
<td>52.9</td>
<td>0.421</td>
<td>126</td>
<td>180</td>
</tr>
<tr>
<td>40</td>
<td>70.9</td>
<td>0.316</td>
<td>108</td>
<td>180</td>
</tr>
<tr>
<td>50</td>
<td>88.9</td>
<td>0.253</td>
<td>90</td>
<td>180</td>
</tr>
</tbody>
</table>

In most experiments, the solvent was 1.5%v/v aqueous acetic acid and methanol with volume proportion of 1:1, unless stated otherwise. Typically, Chi:Ag for molar ratio 5:1 was prepared by dissolving 5.6 x 10^{-2} mol (0.0900 g) of chitosan in 88.8 ml of 1.5% aqueous acetic acid solution and diluted with addition of 90 ml of methanol with vigorous stirring. Then, 1.12 ml (1.12 x 10^{-4} mol) of silver solution was very slowly added to the above solution (total volume became 180 ml) and kept stirring for 1 h. The volume of the acetic acid solution in each chitosan-Ag solution might have slightly varies depending on the volume of sodium borohydride or hydrazine added but generally the volume of 1.5% acetic acid added was not less 40% of the total volume solution except in experiments studying the effect of water content. The silver ions were reduced either by reflux, addition of sodium borohydride, hydrazine or photo-irradiation with a 100 Watt tungsten lamp. After the Chi-Ag was prepared the total volume was measured again to maintain at constant volume. A few drops of methanol were added if the total volume decreased during the preparation.

Another set of experiments were prepared by dissolving 0.036 g of chitosan in aqueous acetic acid solution where water content was varied. The solvent mixture was tabulated in Table 1. The each solution was photo-irradiated for 1 week and the particle size of metal colloids was analyzed by TEM. Similar experiment was performed for Chi:Ag molar ratio of 5:1 and 7:1.

3. RESULTS AND DISCUSSION

Chi-Ag colloids were prepared with various Chi:Ag molar ratios and employing various reduction techniques and different reducing agents. The TEM images were compared to evaluate the appropriate method for preparation of dispersed and finest silver particles. UV-Vis studies were performed to observe silver metal plasmon band progression, at around 400 nm which is characteristic plasmon band for silver colloid

3.1 Spectrophotometry Studies

The UV spectra of Chi-Ag prepared with different reducing agents or techniques were given in Fig.1. It shows that the silver plasmon band was very weak if methanol was used as the reducing agent (Chi-Ag-me) or with photo-irradiation method (Chi-Ag-ir) although the solution has been refluxed or irradiated for 24 h. Whereas, as a comparison, Chi-Pt or Chi-Pd was completely reduced in 0.5 and 3 h respectively. Sodium borohydride and hydrazine which are known as a better or stronger reducing agents than methanol, gave enhance silver plasmon band at around 420-450 nm. Refluxing methanol or photo-irradiation reduced the silver ion slowly resulting in weak intensity of the plasmon band. This suggests that silver reductions with methanol as the reducing agent or with photo-irradiation methods were very slow if it is compared with that of sodium borohydride and hydrazine as the reductant. The order silver plasmon band formation with regard to the type of reducing agent was Chi-Ag-nb > Chi-Ag-hz > Chi-Ag-me ≅ Chi-Ag-ir.

The slower silver reduction by photo-irradiation corresponds to the low energy light employed which was a 100 Watt tungsten lamp. While slow reduction of silver in reflux method was due to low reducing capability of methanol compared to NaBH₄ and N₂H₄. Hydrazine is easier to oxidize by organic electrochemical method with potential as low as 0.3 Volt. In the same method, oxidation of methanol involved 2.5 Volt. Thus reducing capability of hydrazine is higher than methanol. Since the formation of silver plasmon band during photo-irradiation was the slowest among the series of the preparations, the study was focused to the effect of chitosan concentration on the rate of silver colloid band formation. However, the silver band intensity deviation due to the alteration of chitosan concentration was very small and no significant difference in preparation at range of Chi:Ag ratios, 2:1 – 20:1 over 120 minutes of photo-irradiation. Indistinguishable effect of chitosan concentration on formation of silver plasmon band presumably because the increase of Chi-Ag-ir absorbance and the reduction rate are too low to be obvious.

3.2 Particle size and distribution

The particle size and distributions for all monometallic preparations were summarized in Table 2. It shows that
Figure 1. Comparison of UV-Vis spectra Chi-Ag nanoparticles prepared with various reducing agents and techniques, Chi:Ag was 2:1. (1) Chi-Ag-me (5 h reflux), (2) Chi-Ag-ir (5 h photo-ir), (3) Chi-Ag-hz (15 min), (4) Chi-Ag-nb (15 min).

Table 2. Summaries of particle sizes and distributions of Chi-Ag colloidal nanoparticles prepared with various chitosan concentrations, reducing agents and reducing methods.

<table>
<thead>
<tr>
<th>Reduction Methods</th>
<th>Chi:Ag Molar ratios</th>
<th>$d + \sigma / \text{nm}$</th>
<th>$\sigma / d$</th>
<th>Dispersions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBH$_4$, (Chi-Ag-nb)</td>
<td>2:1 (50% H$_2$O)</td>
<td>7.9 ± 2.9</td>
<td>0.4</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>2:1 (50% H$_2$O) 2 weeks</td>
<td>8.5 ± 3.1</td>
<td>0.4</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>5:1 (50% H$_2$O)</td>
<td>10.5 ± 4.8</td>
<td>0.5</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>7:1 (50% H$_2$O)</td>
<td>12.6 ± 5.0</td>
<td>0.4</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>10:1 (50% H$_2$O)</td>
<td>6.8 ± 2.9</td>
<td>0.4</td>
<td>dispersed</td>
</tr>
<tr>
<td></td>
<td>20:1 (50% H$_2$O)</td>
<td>11.5 ± 3.8</td>
<td>0.3</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>30:1 (50% H$_2$O)</td>
<td>8.0 ± 3.6</td>
<td>0.5</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>40:1 (50% H$_2$O)</td>
<td>7.5 ± 2.6</td>
<td>0.3</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>2:1 (50% H$_2$O) 2 weeks</td>
<td>7.9 ± 1.8</td>
<td>0.2</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>5:1 (50% H$_2$O)</td>
<td>8.5 ± 2.1</td>
<td>0.2</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>7:1 (50% H$_2$O)</td>
<td>5.9 ± 1.5</td>
<td>0.3</td>
<td>Dispersed</td>
</tr>
<tr>
<td></td>
<td>7:1 (30% H$_2$O)</td>
<td>8.1 ± 3.8</td>
<td>0.5</td>
<td>Dispersed</td>
</tr>
</tbody>
</table>

generally, Chi-Ag prepared by using sodium borohydride as reducing agent or by photo-irradiation method has dispersed particles. Chi-Ag prepared by refluxing in methanol or by using hydrazine as reducing agent gave less dispersed and more aggregated particles. The particle size of Chi-Ag-me was the largest which range from 21.5 ± 5.3 nm to 29.6 ± 6.1 nm, compared to Chi-Ag particles obtained by other preparation. Chi-Ag-hz, which is prepared with hydrazine as reductant and having more aggregated particles, with range of the individual particle size of 10.4 ± 8.2 nm – 11.6 ± 11.6 nm. The Chi-Ag-hz particles were smaller than...
Figure 2. Representative TEM images and histogram of size distribution of Chi-Ag colloidal nanoparticle prepared with various reducing agents and techniques; (a) Chi-Ag-nb (scale bar : 100 nm), (b) Chi-Ag-hz (scale bar : 200 nm), (c) Chi-Ag-me (scale bar : 200 nm), (d) Chi-Ag-ir (scale bar : 50 nm). Since in some images, the particle size are immeasurable.
Chi-Ag-me but the size distribution was much larger than Chi-Ag-me. The relative standard deviation (σ / d) of Chi-Ag-hz was 1.0 which is fivefold larger that of Chi-Ag-me. The particle sizes of Chi-Ag-nb generally were larger than that of Chi-Ag-ir. Chi-Ag-nb has particle size range in between 6.8 ± 2.9 nm to 12.6 ± 5.0 nm. While Chi-Ag-ir particle size was in range of 4.0 ± 1.1 nm to 8.1 ± 3.8 nm. This is consistent with UV-Vis spectrum pattern that Chi-Ag-ir has much broader band.

Representative TEM images for 2:1 Chi:Ag molar ratio and for each of the preparation technique was shown in Fig. 2. The monographs exhibit the particles of Chi-Ag-nb as very dispersed with average particle size of 7.9 ± 3.0 nm. Chi-Ag-hz particles however, were very aggregated with a few of the aggregated particles attained 10 nm in size but most of which were very large agglomeration. Some of the particles and the aggregation were of irregular shape as shown in Fig. 2 (b), and the individual particles or the aggregation size was immeasurable. The increase aggregation in Chi-Ag-hz was very likely due to the chemical interactions between chitosan and hydrazine. Hydrazine is slightly reactive toward hydroxyl groups which are functional group of chitosan[22]. Several Chi-Ag aggregations might be bridged by hydrazine to form larger aggregation.

Chi-Ag-me particles have spherical shape and some formed nano-sphere. The average particle size was 29.6 ± 6.0 nm and relatively less dispersed and the size becomes smaller at higher molar ratio of Chi:Ag as shown in Table 2. Although Chi-Ag-me particles are relatively large, the particles have narrowest size distribution with σ/d of 0.2. The smaller silver particle size with narrow size distribution and very dispersed particles were obtained when it was prepared by photo-irradiation. The average particle size of Chi-Ag-ir was 3.2 ± 1.1 nm. The Chi-Ag-ir clusters grow slowly and at the time of observation, the particles were likely still growing and it takes longer time to (Oswald) ripen compared to those prepared by other preparation techniques. Among the series of preparations, photo-irradiation method gave smallest size and narrower size distribution of silver colloidal nanoparticles, however, as the silver reduction was very slow, the silver particles continuously grow.

Lower in particle size of Chi-Ag-ir compared to others might subject to their difference in reduction rates. It was observed that the size doubled from 3.2 to 7.9 nm after 2 weeks of preparation (Table 2, entry; photo-irradiation, row 4). This was similarly observed for the other preparations; hydrazine, methanol and sodium borohydride as the reductants. Particularly in hydrazine method, the silver sol precipitated out in few weeks (Table 2, entry; Chi-Ag-hz, row 2). While higher hydrazine mol proportion led to precipitation of Chi-Ag-hz. In sodium borohydride method, where the silver reduction was supposedly faster, the particle growth was still observed but at a slower pace compared to the other preparations (Table 2, entry; Chi-Ag-nb, row 2). The particle growth of Chi-Ag-nb corresponds well to the UV-Vis plasmon change as shown in Fig. 3. The plasmon band intensity increased gradually and the band shifted slightly to higher wavelength, inferring the effect of the particle aggregation[11,14]. The instability of silver particles has been addressed in previous publication[23]. The better reducing properties of sodium borohydride compared to hydrazine as reducing agent was consistent with previous report employing aniline as the stabilizer for silver sol in which the particles were unstable and grow to the size of 125 nm[24].

Table 2 displays that at 2:1 Chi:Ag molar ratio and with addition of 30% of water, Chi-Ag-ir gave the smallest silver particle size. There has been no further
Attempts to obtain uniform size by avoiding silver growth techniques were reported by others. Particles ripening using nucleation and template-directed described in previous study. The consequences included the alteration of the solubility of silver ion and chitosan and interaction of chitosan with reducing agent such as hydrazine as solubility of silver ion and chitosan and interaction of chitosan on silver particle morphology. This because chitosan as stabilizer for silver nanoparticles is acceptable and exhibits better stabilizing quality than those reported earlier.

4. CONCLUSIONS

Chitosan-stabilized silver colloidal nanoparticles were prepared in relatively low Chi:Ag molar ratio. The Ag(I) ions were reduced in chitosan matrix using photo-irradiation, refluxing (methanol) and chemical reductants technique. It was very slow if it is reduced by photo-irradiation or refluxing (methanol) techniques compared with the other preparation employing chemical reductant i.e. sodium borohydride or hydrazine as the reducing agents. The silver colloidal nanoparticles were aggregated, large in size with broad size distribution if it is prepared by using hydrazine as the reducing agent. Chitosan colloidal-silver nanoparticles prepared by using methanol as reducing agent are less dispersed, large in size but narrow size distribution. Sodium borohydride and photo-irradiation method gave smaller and narrow size distribution of silver particles compared to the other reducing agent or technique. Photo-irradiation using low energy of light (a 100 Watt tungsten lamp) gave smallest silver particles, more dispersed and narrower size distribution compared to other method but slower silver reduction and silver particles ripening are noticeable.

REFERENCES


