

PHOTOCHEMICAL REDUCTION OF SILVER NITRATE TO NANO SILVER USING STANNOUS CHLORIDE, CTAB AND DAYLIGHT IRRADIATION

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ABSTRACT

Silver nanoparticles (NPs) were synthesized and stabilized by a simple method in aqueous solution, by the reduction of silver nitrate with stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and cetyl trimethyl ammonium bromide (CTAB) through day light irradiation. Thereby, the silver nanoparticles were colloidally stabilized by CTAB as a surfactant. The synthesis of silver NPs with different size were possible by changing the reaction conditions such as reagent ratio. The silver NPs were characterized by Dynamic Light Scattering (DLS) and UV-visible spectroscopy. A very strong plasmon resonance peak at 400-500 nm in the UV-visible spectra is a clear consequence of the silver NPs production. The synthesized silver NPs showed good stability by using CTAB.

Key words: Silver nanoparticles (NPs), Stannous chloride, Cetyltrimethyl ammonium bromide.

INTRODUCTION

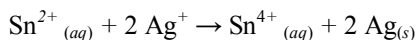
Silver NPs, a particle of Ag element, is a new class of material with remarkably different physicochemical characteristics such as increased optical, electromagnetic and catalytic properties from the bulk materials [1-2]. NPs with at least one dimensional of 100 nm or less have unique physicochemical properties, such as high catalytic capabilities and ability to generate reactive oxygen species (ROS) [3]. Silver in the form of NPs could be therefore more reactive with its increased catalytic properties and become more toxic than the bulk counterpart. Further more toxicity is presumed to be size and shape dependent, because small size NPs (e.g., <10 nm) [4-5], may pass through cell membranes and the accumulation of intracellular NPs can lead to cell malfunction.

Nano silver (silver nanoparticles, Ag NPs) have a wide range of application including spectrally selective coating for solar energy absorption [6], catalysis in chemical reaction [7], surface-enhanced raman scattering (SERS) for imaging [8], and antimicrobial sterilization [9-10]. Because of their effective antimicrobial properties and low toxicity toward mammalian cells, silver NPs

have become one of the most commonly used nanomaterial in consumer products [11-12]. These NPs will likely enter the sewage pipes and the wastewater treatment plants (WWTPs).

Several methods have been employed to synthesize silver NPs [13]. Among them, the chemical reduction methods has been extensively investigated because of its simplicity of performance and mild conditions [13]. Usually, the chemical reduction is composed of silver nitrate as a precursor, reducing agent, and stabilizer [14]. The mechanism of silver NPs formation from solution has been elucidated [15]. Metal colloids are formed their ions in solutions through nucleation, followed by the growth step [16]. As reducing agent for silver ion to silver particles, several reducing agents, such as sodium citrate [17], ascorbic acid [18], potassium bitartrate [19], hydrazine [20], and polyethylene glycol [21], can be used. The strong reducing agent leads to smaller particle formation, in comparison to a weak reducing agent [22].

Stannous chloride($SnCl_2 \cdot 2H_2O$) is widely used as a reducing agent (in acid solution), and in electrolytic baths for tin-plating [23]. This is seen in its use for silvering mirrors, where silver metal is deposited on the glass:



Stannous chloride also used as a mordant in textile dyeing because it gives brighter colors with some dyes [24]. This mordant has also been used alone to increase the weight of silk. A related reduction was traditionally used as an analytical test for $Hg^{2+}_{(aq)}$. Stannous chloride can be used to test for the presence of gold compounds. $SnCl_2$ turns bright purple in the presence of gold [25]. In organic chemistry, $SnCl_2$ is mainly used in the Stephen reduction, whereby a nitrile is reduced (via an imidoyl chloride salt) to an imine which is easily hydrolysed to an aldehyde. Additionally, $SnCl_2$ is used to selectively reduce aromatic nitro groups to anilines.

$SnCl_2$ also reduces quinones to hydroquinone [26]. Stannous chloride is also added as a food additive with E number E512 to some canned and bottled foods, where it serves as a color-retention agent and antioxidant

Due to the high reactivity of silver NPs are not stable and rapidly undergo agglomeration [27]. The stabilizing agent are used to separated the particles to prevent agglomeration [28]. The surfactant or polymers, such as cetyltrimethyl ammoniumbromide (*CTAB*), liposome [29], poly vinyl pyrrolidone (*PVP*), are usually used as stabilizers to control the size of NPs [30].

To our knowledge there is no report on synthesise of silver nano particles by $SnCl_2$. Thus we developed a simple method to synthesise silver NPs on aqueous solution with stannous chloride as a reducing agent and *CTAB* as a stabilizer. UV-vis spectroscopy and Dynamic Light Scattering (DLS) were used

to identify the products and we found that well-dispersed silver NPs in solution obtained.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Materials. Silver nitrate (AgNO_3 extra pure, >99.8%) was used as a precursor for the preparation of silver NPs, and stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), as a reducing agent, was purchased from Merck (Frankfurt, Ludwigshafen, Germany). CTAB from Merck (Darmstadt, Germany) was used as surfactant for stabilizing silver NPs.

Synthesis of silver NPs. The preparation of silver NPs was carried out by a simple, environment-friendly method in an aqueous solution. The CTAB was added to an aqueous solution of silver nitrate with rapid stirring. Then a freshly prepared stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) solution was added by drop-wise addition to the mixture under vigorous stirring (approximately 3500 rpm) for 10 min at room temperature in dark condition. The reaction solution was then irradiated with daylight for different times. The silver nitrate solution was reduced and silver NPs formed. In this method, $[\text{CTAB}]/[\text{AgNO}_3]$, is the influencing factor in the synthesis of silver NPs. In order to obtain particles with different size the $([\text{AgNO}_3]/[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}])$ is variable. The ratio of various chemicals is presented in *Table 1*.

Table 1 – Composition of variation solutions ($[\text{AgNO}_3] = 1\text{mM}$)

Solution	$[\text{CTAB}]/[\text{AgNO}_3]$	$[\text{AgNO}_3]/[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}]$
1	0	13
2	0	8.5
3	0	6.5
4	0	4.5
5	1	13
6	1	8.5
7	1	6.5
8	1	4.5
9	2	13
10	2	8.5
11	2	6.5
12	2	4.5
13	3	13
14	3	8.5
15	3	6.5
16	3	4.5

Instrumentation. Silver NPs were characterized by dynamic light scattering (DLS), using the zetasizer nano HPPSv420 (Malvern Instruments, Ltd., Malvern, UK) at 25°C. The hydrodynamic diameter (z-average), mode values of the particle size, polydispersity index, and width distribution of the particle

were determined. The diameter correlates to the effective particle movement within a liquid, which is the particle diameter plus electrical double layer. The hydrodynamic diameter is described as the Stokes-Einstein equation [31].

$$d_H = kT/3\pi\eta D$$

Where d_H is the hydrodynamic diameter, k is the Boltzmann constant, T is the temperature, η is the solvent viscosity, and D is the diffusion coefficient.

The ultraviolet (UV) absorption spectrums of different samples were taken at room temperature on a (Optizen, Mecasys, Deajeon, Korea, 2120 UV) UVspectrophotometer with a 2 nm resolution. The spectrum wavelengths were between 200 and 600 nm and use a glass cuvette with a 1 cm optical path.

RESULTS AND DISCUSSION

UV-visible spectrum of silver NPs analysis

In noble metals, decreasing the size to below the electron mean free path (i.e., the distance the electron travels between scattering collisions with the lattice center) gives rise to intense absorption in the visible near UV range. The UV-extinction spectra characteristics, such as the red or blue shifting, maximum absorption intensity, and full width at half maximum (FWHM) of absorption peaks, have proven to be quite sensitive to the shape, size, size distribution of silver NPs, stabilizer, and refractive index of solution [32].

Formation of silver NPs by ambient light illumination. In the presence of ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), $\text{AgNO}_3/\text{CTAB}$ solution remains colorless and no significant change can be detected in the absorption spectra of the solution in the absence of daylight irradiation. This indicates that reduction of Ag^+ ions does not take place. However, the clear solution will gradually turn yellow and then reddish yellow when a solution is irradiated by daylight.

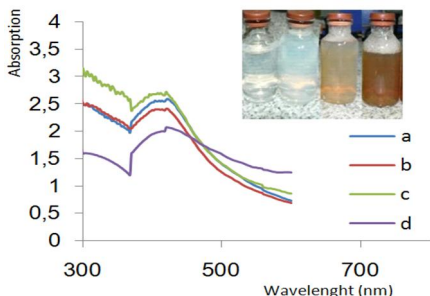
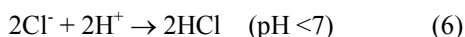
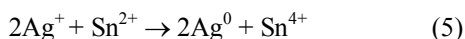
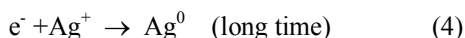
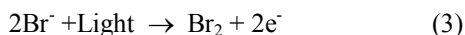
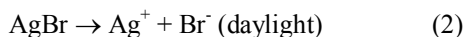


Fig. 1 – UV-vis absorption of solution 12 irradiated via daylight for different times or in the dark condition. a) freshly prepared, b) in dark for 24 h, c) irradiated via daylight for 24 h and d) irradiated via daylight for 2 h

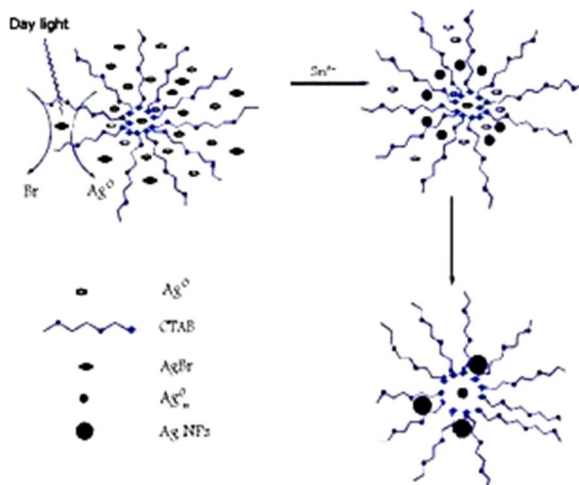
A characteristic silver plasmon band appear at 400-500 nm on the absorption spectra, indicating the formation of metallic silver in the solution. Interestingly, no color change take place if solutions is kept in the dark, and no silver plasmon band can be detected on the absorption spectra (*Figure 1*). When the $[\text{CTAB}]/[\text{AgNO}_3]$ ratio is decreased from 2 to 1, the formation of a silver colloid occurs instantly. The rapid formation of metallic silver confirmed by UV spectroscopy. Such a sensitive

response to the daylight implies that this method may find potential application in the photographic and micropatterning fields. When the ratio increased up to 2 and 3, no formation of silver NPs was observed even in the higher concentration of $(\text{SnCl}_2 \cdot 2\text{H}_2\text{O})$ under daylight irradiation.

It has been reported that cationic surfactant (CTAB), could slowly form Ag^+/CTAB , AgBr/CTAB , and AgBr structures through their quaternary ammonium groups [33-34]. In fact the reduction of Ag^+ ions in the solution can only proceed under daylight irradiation according to equation 1-6.



Based on the observation and characterization results, we propose a possible mechanism to explain the formation of silver NPs in the system (Scheme 1).



Scheme 1 – Schematic illustration of the possible formation process of silver NPs via daylight irradiation

First, Ag^+ ions are incorporated in the micelles of CTAB and formation Ag^+/CTAB , AgBr , and AgBr/CTAB structures [33-34]. This process of incorporation and formation structures causes dramatic change to the UV spectra as shown in *Figure 1*. This process is similar to the formation of the metal silver during the conventional photographic process where silver halide is used as a semiconductor to capture incident light [35]. Silver cluster will then form through the agglomeration of silver atoms and Ag^+ ions. The reduction of Ag^+ ions and the following agglomeration in the system may proceed as follows:



The CTAB molecules can stabilize Ag^+ through complexation. This complexation inhibits the agglomeration of silver clusters and thus prevents the uncontrolled growth of the silver NPs [36]. Thus CTAB plays multiple roles in the formation of the silver NPs:

- 1) To induce the reduction of Ag^+ ions by forming AgBr .
- 2) To control the growth of silver NPs through complexing with silver cluster.
- 3) To prevent the agglomeration of silver NPs through steric hindrance.

Effect of concentration of $[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}]$

Figure 2 shows the UV-vis absorption of silver NPs solution with different concentration of stannous chloride.

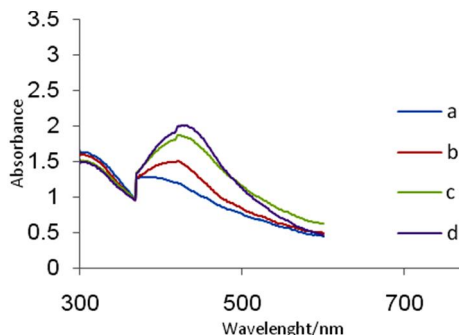


Fig. 2 – UV-vis absorption of solution with $([\text{CTAB}]/[\text{AgNO}_3]=2)$, illuminated via day light for 24 h. a) solution 9 b) solution 10 c) solution 11 d) solution 12

With the increasing concentration of stannous chloride, there was a red shift in the absorption peak of spectrum. It has long been known that the maximum absorption peak will shift to longer wavelength (red shift) when the particle size becomes larger [36].

In addition, increasing concentration of stannous chloride causes the formation of more silver NPs that is well clear from *Figure 2*.

Effect of irradiation time

The photochemical formation of silver NPs was monitored by taking UV-vis absorption spectra as a function of irradiation time (Figure 1). After 2 h an absorption peak at about 400 nm can be observed. On increasing the irradiation time, the absorption peak gradually increase and shifts toward longer wavelengths. This is characteristic of increase in the concentration and size of silver NPs. The amount of silver reduced and the extent of silver agglomeration increase with the irradiation time. The rate of silver NPs formation is function of CTAB concentration. It is readily noticed that a higher concentration of CTAB ($[\text{CTAB}]/[\text{AgNO}_3]=2$ and 3) result in a slower photochemical process, which implies the influence of CTAB in silver reduction.

DLS of silver NPs

The z-average and poly dispersity index of silver NPs are demonstrates in *Figure 3* and *Figure 4*. The z-average of NPs was reduced by using CTAB, and the smallest NPs were synthesized by presenting the lowest concentration of CTAB ($[\text{CTAB}]/[\text{AgNO}_3]=1$) in the colloidal solution.

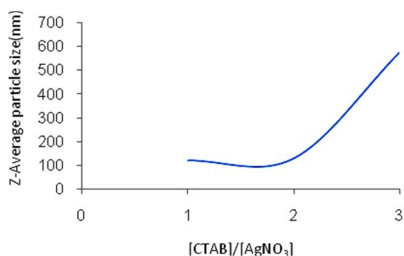


Fig. 3 – Effect of various concentration of CTAB on z-average of silver NPS

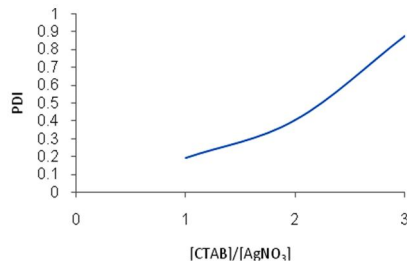


Fig. 4 – Effect of various concentration of CTAB on PDI of silver NPS

In addition, CTAB concentration also effective on the poly dispersity index of silver NPs. The lowest concentration of CTAB has the lowest poly dispersity index.

The lowest value of poly dispersity index of silver NPs leads to obtain a narrow size distribution. An increase of CTAB concentration also leads to the increase poly dispersity index. This means that the particles with wide range of size are formed at high concentration of CTAB.

CONCLUSIONS

A novel method has been developed to prepare silver NPs through reduction by SnCl_2 under daylight irradiation. The effectiveness of daylight was clearly shown in that no silver particles has been synthesized without daylight. A possible mechanism is proposed to explain the formation of silver NPs. Also, silver NPs have been stabilized by CTAB. Further, the size and poly dispersity index depend on the CTAB concentrations.

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