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Thermal decomposition as route for silver nanoparticles

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Abstract Single crystalline silver nanoparticles have been synthesized by thermal decomposition of silver oxalate in water and in ethylene glycol. Polyvinyl alcohol (PVA) was employed as a capping agent. The particles were spherical in shape with size below 10 nm. The chemical reduction of silver oxalate by PVA was also observed. Increase of the polymer concentration led to a decrease in the size of Ag particles. Ag nanoparticle was not formed in the absence of PVA. Antibacterial activity of the Ag colloid was studied by disc diffusion method.

Keywords Ag nanoparticles · Synthesis · Silver oxalate · Thermal decomposition · *E. coli*

Introduction

Synthesis of silver nanoparticles is a significant area of research, because Ag nanoparticles have potential applications in various fields such as biochemistry, environment, medicine, catalysis, electronics and optics [1–4]. Particularly, the recent finding revealed that Ag nanoparticles can bind to the HIV [5]. Even though many methods have been reported in the literature, the interest in the field of genesis of Ag nanoparticles has not diminished. Among the various methods available, thermal decomposition of metal complexes is one of the possible ways of producing metal nano structures [6]. If the decomposition temperature of metal complexes is low and the product is metal, this reaction can be utilized for the synthesis of nanoparticles. It has been known that silver oxalate ($Ag_2C_2O_4$) decomposes at around 140 °C and yields metallic silver and CO_2 [7]. In this paper, the synthesis of Ag nanoparticles by thermal decomposition of silver oxalate ($Ag_2C_2O_4$) in water and ethylene glycol media has been explored.

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Experimental

Silver oxalate was prepared by mixing 50 mL of 0.5 M $AgNO_3$ solution with 30 mL of 0.5 M oxalic acid. The white precipitate formed was filtered, washed with distilled water, dried at 60 °C and stored in a dark bottle [7]. Formation of $Ag_2C_2O_4$ was confirmed by TGA. To 40 mL of water, required amount (for different ratios) of polyvinyl alcohol (PVA) (M.W = 125,000) was added and stirred. After the complete dissolution of PVA, 0.05 g of $Ag_2C_2O_4$ was added, stirred for 10 min and purged with N_2. This mixture was refluxed, in a flow of N_2 gas, at 100 °C for 3 h in an oil bath. The formation of yellow colour colloid was observed in the reaction mixture. The N_2 gas from the outlet was passed through a 10% baryta solution to confirm the evolution of any CO_2 during the formation of the nanoparticles. Then it was cooled to room temperature under N_2 atmosphere. The resultant solution was centrifuged for 5 min at 1,000 rpm to separate the yellow Ag nano powder. Experiments were carried out with 1:1, 1:2, 1:5 and 1:10 weight ratios of $Ag_2C_2O_4$ and PVA. The same experimental procedure was employed in ethylene glycol

medium with 1:5 weight ratio of $Ag_2C_2O_4$ and PVA. The silver colloid was characterized by UV–visible spectroscopy, Transmission electron microscopy (TEM), SAED patterns and EDAX spectrum. The antibacterial activity of the Ag nanoparticles was also studied.

Disc diffusion method was followed in order to study the antibacterial activity of Ag nanoparticles [8]. Luria–Bertani (LB) medium has been prepared as follows: 1 g of tryptone, 1 g of NaCl, 0.5 g of yeast extract and 2 g of agar are taken in 100 mL of water. Before starting the antimicrobial activity study, the petri dishes were sterilized in an autoclave for 30 min. LB medium was transferred to the properly sterilized petri dish in the laminar flow. After 2 h, *E Coli* (*Escherichia Coli*) inoculums of optical density 0.6 were dispersed on the LB medium. For this study, the Ag colloid prepared in water with 1:5 ratio was used. Three sets of experiments were carried out using the original colloid, ten times diluted colloid and a blank without the Ag colloid. A filter paper disc of 5 mm diameter was dipped into the Ag colloid for 5 min and placed in the centre of petri dish where inoculums and LB medium are present. These dishes were kept in the incubator at 37 °C for 24 h. Then the growth of the *E. coli* in the dishes was monitored.

UV–visible spectra were recorded using Jasco V-530 spectrophotometer. TEM pictures were recorded with Philips CM12 microscope working at a 100 kV accelerating voltage. TGA and DSC analyses have been carried out with Perkin Elmer TGA 7 and Perkin Elmer DSC 7 respectively. XRD powder pattern was collected from Shimadzu X-ray diffractometer model XD 01 using Cu Kα radiation (λ = 1.5405 Å).

Results and discussion

Thermal behavior of silver oxalate prepared has been analyzed using TGA and DSC techniques under nitrogen atmosphere. Thermal decomposition of $Ag_2C_2O_4$ occurred around 140 °C which is in agreement with the reports in literature [7]. TGA profile is shown in the Fig. 1. The solid mass left after weight loss has been calculated and it corresponds to the weight of metallic silver i.e., 71.0% and this agrees with the theoretical value for silver oxalate decomposition.

In DSC profile, an exothermic peak has been observed around 140 °C. This shows that decomposition of silver oxalate is an exothermic reaction [8]. Along with TGA analysis, DSc profile yields complementary evidence that the thermal decomposition of silver oxalate yield the elementary silver at

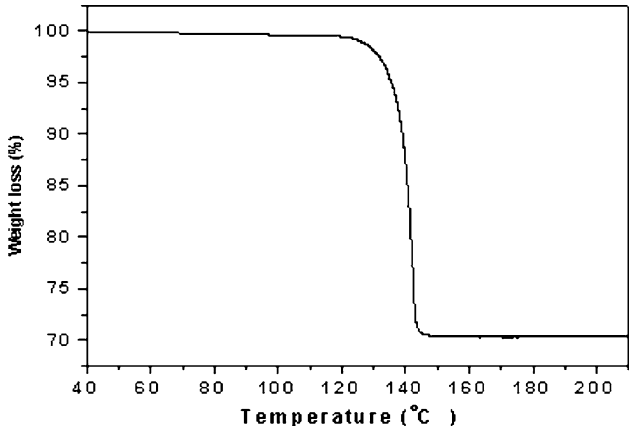

Fig. 1 Thermal gravimetric analysis of $Ag_2C_2O_4$ recorded at the scan rate of 1 degree per minute

140 °C. This low temperature decomposition of $Ag_2C_2O_4$ is due to the favorable reducing capacity of oxalate dianion ($E^0_{(CO_2/C_2O_4^{2-})} = -0.49$ V) [9] and favorable oxidizing power of Ag^+ ($E^0_{Ag+/Ag} = 0.799$)[10]. It is explained that breakage of C–C bond is the first step in the decomposition of silver oxalate. The interstitial Ag^+ cations facilitate the cleavage of the C–C bond in $Ag_2C_2O_4$ [11, 12]. Since Ag^+ is reduced by oxalate di anion, formation of CO_2 is favorably taking place and electrons are transferred to Ag^+.

$$Ag_2C_2O_{4(s)} \xrightarrow[N_2,\Delta]{} 2Ag_{(s)} + 2CO_{2(g)} \quad (1)$$

UV–visible spectra of silver colloids prepared from the thermal treatment of silver oxalate yields the surface plasmon bands in the range of 409–427 nm [13].

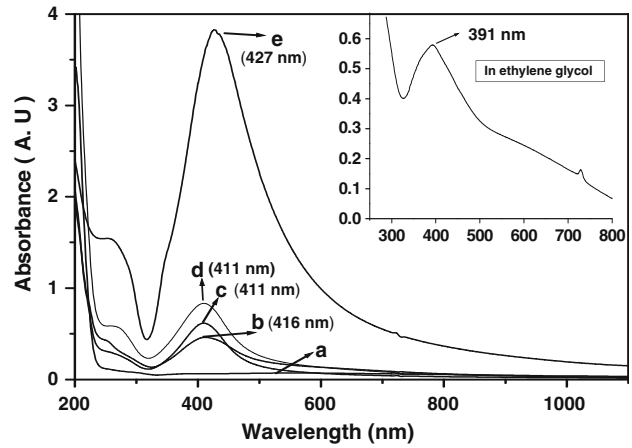

Fig. 2 UV–visible spectra of silver colloids with various $Ag_2C_2O_4$ to PVA weight ratios (**a**) 1:0; (**b**) 1: 1; (**c**) 1:5; (**d**) 1: 10; (**e**) 1: 5 heat treated for 5 h. Inset: Ag colloids synthesized in ethylene glycol (1:5)

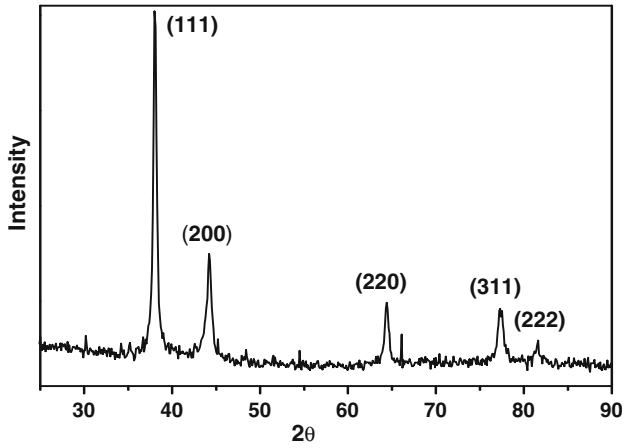

Fig. 3 XRD powder pattern of the Ag powder produced from the thermal decomposition of $Ag_2C_2O_4$ in aqueous medium without PVA

These are shown in Fig. 2. Bulk Ag particles are formed in the case where PVA is not used and the corresponding XRD powder pattern is shown in Fig. 3.

This observation reveals the formation of Ag nanoparticle during the decomposition of $Ag_2C_2O_4$ in N_2 atmosphere. It is observed that PVA, the capping agent, is necessary for the formation of Ag nanoparticle. However, in air atmosphere, silver nanoparticles have not been observed. When the refluxing has been carried out for <3 h, one could not observe any evolution of CO_2 indicating that the formation of the silver colloid is by chemical reduction. PVA acts as the reducing agent. The surface plasmon band observed confirms the presence of Ag nanoparticles. This indicates the possibility of chemical reduction of $Ag_2C_2O_4$ by PVA. Alcohol functionality of PVA may be acting as a reducing center under thermal conditions [14]. This can be explained by the following reaction.

$$Ag_2C_2O_4 + 2\text{-}(H_2C\text{-}\underset{|}{\overset{OH}{CH}})\text{-} \xrightarrow{\Delta} 2\,Ag + \text{-}(H_2C\text{-}\underset{||}{\overset{O}{C}})\text{-} + H_2C_2O_4 \quad (2)$$

On the contrary, when the experiment is continued for a longer period, one could observe the characteristic white precipitate of $BaCO_3$ obtained, on passing the gas outlet through the baryta solution. This indicates that under these conditions thermal decomposition is possible leading to the evolution of CO_2 as per the equation 1.

Ag colloid prepared by refluxing for 5 h has given rise to the formation of colorless precipitate in $Ba(OH)_2$ solution. This implies that decomposition of silver oxalate takes place after 3 h of refluxing. In this case, both chemical reduction [15] as well as thermal decomposition has taken place to yield Ag

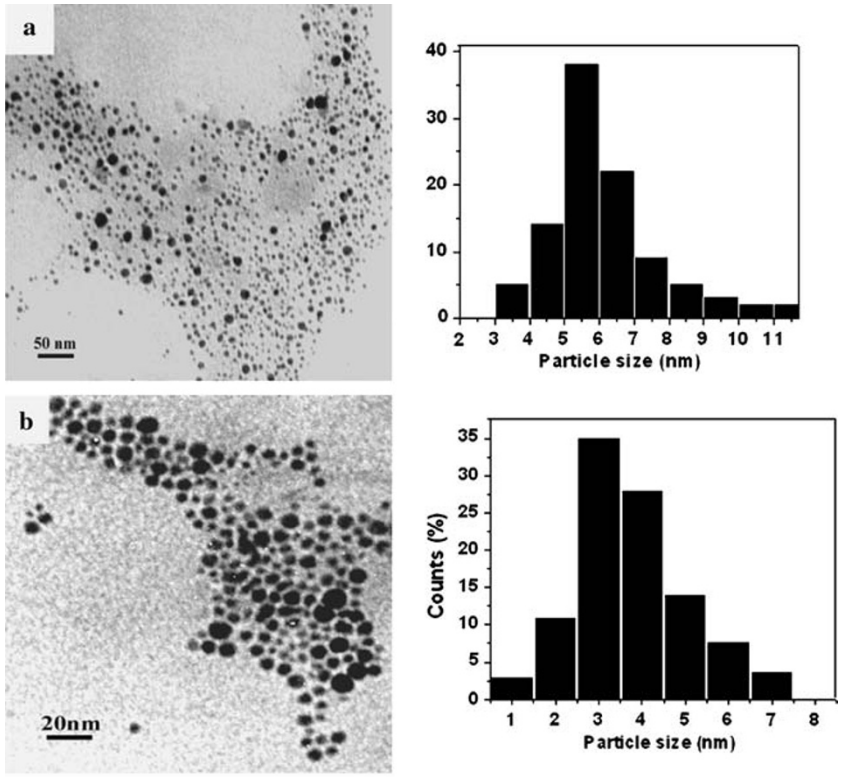

Fig. 4 TEM pictures of Ag nanoparticles prepared in water with $Ag_2C_2O_4$ to PVA weight ratio (**a**) 1: 1; (**b**) 1:5 with heat treatment for 3 h. The corresponding particle size distributions are shown along side

nanoparticles. Moreover, the intensity of the surface plasmon band pertaining to Ag colloid derived from the decomposition method is higher than the colloid formed due to chemical reduction alone. This shows that more amount of Ag colloid was formed while it was prepared by 5 h of heat treatment.

TEM pictures of Ag colloids are shown in Fig. 4 and 5. The particle size distributions are shown along side with the corresponding pictures. Fig. 4(a) shows TEM picture of Ag colloid formed with 1:1mixtures of $Ag_2C_2O_4$ and PVA and it can be observed that particles are spherical and average particle is in 4–7 nm range. TEM picture shown in the Fig. 4(b) corresponding to Ag nanoparticles derived from the 1:5 weight mixtures of $Ag_2C_2O_4$ and PVA reveals the spherical particles with the average particle size of 2–4 nm. This shows that as the PVA concentration is increased, the average particle size decreases. This is supported by the corresponding surface plasmon spectrum also. As PVA concentration in the reaction mixture increases, λ_{max} of surface plasmon band shifts to lower wavelength region. The lower the $\lambda_{max,}$ the lower will be the particle size. However, TEM picture shown in Fig. 5(a) pertains to the Ag colloid formed by thermal decomposition and chemical reduction, and it shows the presence of nanoparticle along with some micron level particles. But, as compared to smaller particles, the number of bigger particles is much less. Since the decomposition is so fast and exothermic, the agglomeration of particles, in this case, is possible. Hence, the bigger particles have been formed due to agglomeration. The presence of Ag is confirmed by the SAED (Selective area electron diffraction pattern) and EDAX spectrum (Fig. 6). Spot pattern obtained for Ag nanoparticles shows the single crystalline nature.

In order to understand the effect of the reaction medium, the same reaction has been carried out in ethylene glycol with $Ag_2C_2O_4$ to PVA ratio of 1:5. A greenish yellow colloid is formed and its surface plasmon band is observed at 391 nm. TEM picture shown in the Fig. 5(b) corresponds to the Ag colloid

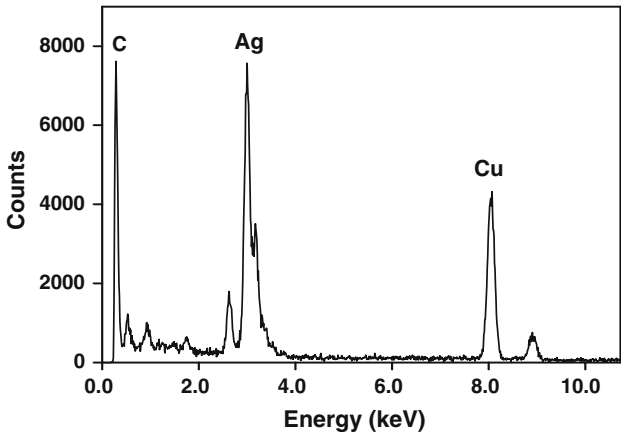

Fig. 6 EDAX spectrum of silver nanoparticles prepared by thermal decomposition

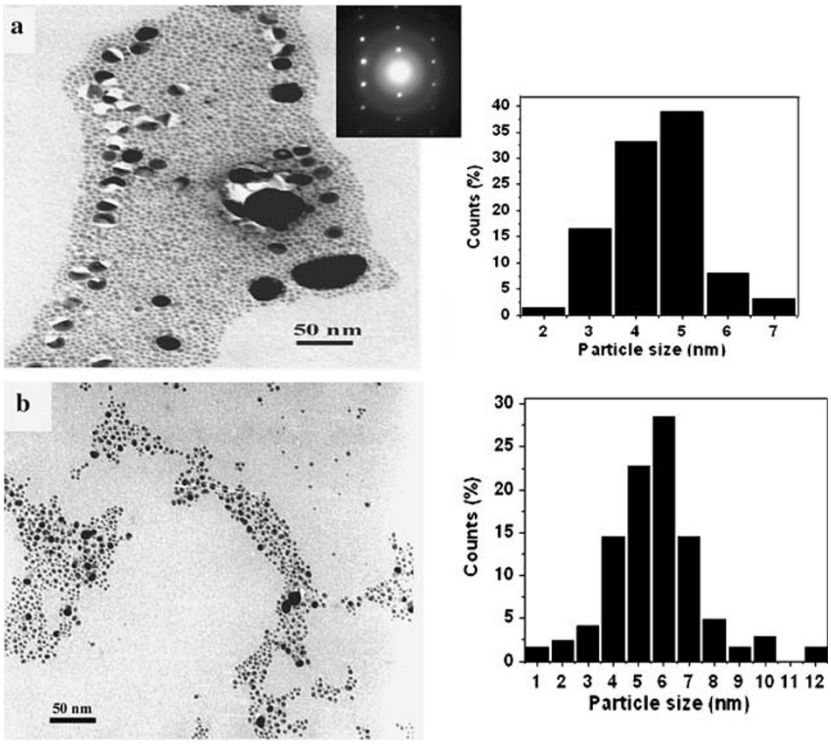

Fig. 5 TEM pictures of Ag nanoparticles synthesized with $Ag_2C_2O_4$ to PVA weight ratio (**a**) 1:5 heated for 5 h in water (SAED pattern is shown); (**b**) in ethylene glycol heated for 20 min. The corresponding particle size distributions are shown along side

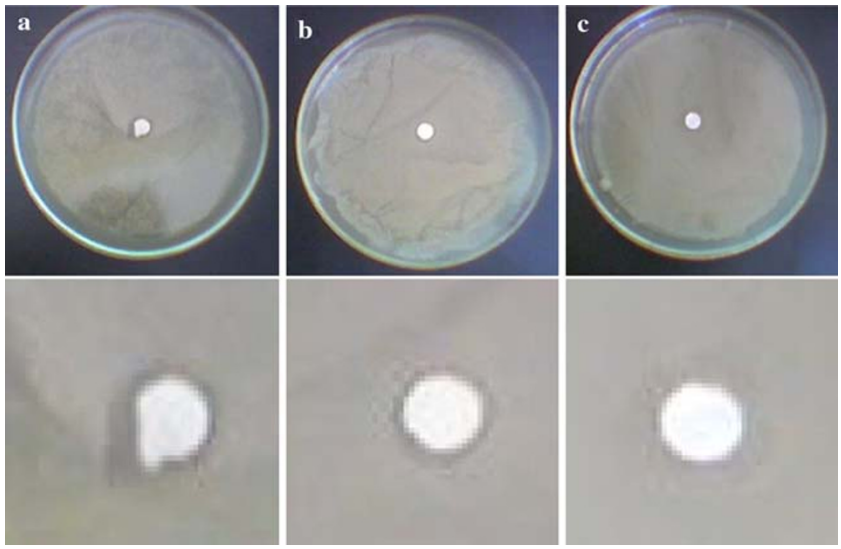

Fig. 7 The photographic pictures of dishes used for antimicrobial study. (**a**) Ag nanoparticles synthesized using 1:5 weight of $Ag_2C_2O_4$ and PVA mixture in water; (**b**) 10 times diluted; (**c**) reference (No Ag colloid). Magnified zone of requisite area of dishes are shown below the corresponding dishes

formed in ethylene glycol, and shows the spherical particles of 4–7 nm. The decomposition occurred in water and ethylene glycol after 3 h and 20 min respectively. This difference is due to the boiling point of the medium. The boiling points of water and ethylene glycol are 100 °C and 198 °C [16] respectively. The decomposition of silver oxalate in ethylene glycol is more facile than in water.

The results for the antibacterial study carried out by disc diffusion method are shown in Fig. 7. The dishes, in which the antibacterial study of Ag nanoparticles is carried out, are shown and the dark zone can be observed around paper disc, which contains silver nanoparticles. This dark zone is known as inhibition zone where the growth of *E. Coli* was prevented. As can be seen from the Fig. 7, the area of inhibition zone is more for Ag colloid (a) prepared by decomposition using 1:5 of $Ag_2C_2O_4$ and PVA reaction mixture than that of 10 times diluted Ag colloid (b). Fig. 7(c) is reference, which contains only PVA treated under the same condition. This reveals that Ag colloids prepared by this method show antimicrobial activity. These Ag colloids stored in air-tight bottles are stable even after a year.

Conclusions

Thermal decomposition of silver oxalate was utilized to synthesize the single crystalline Ag nanoparticles in large amount using PVA as a capping agent. Since the reaction mixture was heated for a period, the chemical reduction also has taken place in parallel. However, the amount of Ag colloid formed by decomposition is higher than that of chemical reduction. PVA plays a major role in this thermal decomposition method and its concentration is an important parameter to determine the particle size. The thermal decomposition of $Ag_2C_2O_4$ was quicker in ethylene glycol medium than the aqueous medium. The Ag nanoparticle colloid was found to be potential antibacterial agent.

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