

# Synthesis of silver nanoparticles by chemical reduction method and a comparison study of silver-filled epoxy thin film composites

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**Abstract.** Uniform, well-dispersed, silver nanoparticles (AgNPs) were prepared by a simple chemical reduction method. The particles were synthesized via the reduction of AgNO<sub>3</sub> by trisodium citrate and ascorbic acid as a surfactant. The resulting AgNPs were characterized by x-ray diffraction analysis (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). It was found that the size of the AgNPs ranged from 35-80 nm, with an average of 50 nm. The as-synthesized AgNPs were then dispersed into an epoxy matrix, to form electrically conductive adhesives (ECAs), in the form of a thin film. For comparison, ECAs produced using commercial silver particles, e.g. silver flakes and silver nanoparticles, were prepared at a constant filler loading, and the electrical conductivity was observed. It was found that the as-synthesized AgNPs showed the highest electrical conductivity ( $2.53 \times 10^{-1}$  S/cm) in comparison to the ECAs prepared using commercial particles.

## Introduction

For several decades, electronics industries have used silver flakes (AgF) with a typical size range 1-10 $\mu$ m as the filler in electrical conductive adhesives (ECAs) [1]. However, recent developments in the field of nanotechnology have led to a renewed interest in the potential application of nanoparticles as replacement filler to the current silver flakes. Theoretically, smaller sizes will reduce the quantity of conductive filler required to provide the desired electrical conductivity. However, the most crucial problems facing the usage of nanoparticles, is their dispersion throughout the matrix; due to their tendency to agglomerate, which restricts their usage within ECAs.

As size distribution of the conductive filler is one of the factors in improving the performance of the ECAs, a method to synthesis silver nanoparticles should be developed. In recent years, many chemical methods for synthesis of silver nanoparticles have being reported [2-4]. However, chemical reduction is the most commonly used, due to its simplicity. This technique also enable the variation in molar concentration of reactant, dispersant and feed rate of reactant in order to produce silver nanoparticles with controlled particle size, shape and particle size distribution. In this paper, we describe a simple, low cost, and partially green method, to synthesize silver nanoparticles. This synthesis method is considered partially green as we use ascorbic acid which is one form of Vitamin C that can be derived from glucose. It also has been widely used as reducing agent in synthesis process. However, there is no work reported the use of ascorbic acid as surfactant especially in synthesis of silver particle. Therefore, in present work, ascorbic acid has been used as a surfactant, rather than as reducing agent in order to prevent the aggregation of metal particles. The effects of the combined trisodium citrate and ascorbic acid on the AgNPs produced were characterized by XRD, whilst particle morphology and size were observed by SEM and TEM, respectively. As comparison, besides the as-synthesized AgNPs, commercial silver flakes and AgNPs were also used

to prepare the ECA thin film. It was found that with controlled particle size distribution and the dispersion of the as-synthesized AgNPs within an epoxy matrix, an improved conductivity of ECAs could be achieved.

## Experimental

Silver nitrate ( $\text{AgNO}_3$ ) was used as a starting material while Trisodium citrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ ) and Ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) were used as the reducing agent and surfactant, respectively. An optimum condition of 0.9mM  $\text{AgNO}_3$ , 8.0mM  $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ , and 1.0mM  $\text{C}_6\text{H}_8\text{O}_6$  was applied in this study, with some modification to the existing method reported by Dadosh [5]. In this study, 80 ml of  $\text{AgNO}_3$  was first heated to  $60^\circ\text{C}$  and was then added (with vigorous stirring) into 20 ml of a  $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$  and  $\text{C}_6\text{H}_8\text{O}_6$  solution, that was pre-heated to  $60^\circ\text{C}$ . The mixture then was stirred for 20 minutes. After that, the heating was stopped and the solution was cooled at room temperature with continuous stirring. The as-synthesized AgNPs colloid was characterized by XRD (model D5000 Siemens Diffractometer) with 0.15405 nm Cu  $K\alpha$  radiation. The size and morphology of the Ag nanoparticle produced were studied by TEM (model Philips CM12 equipped with Docu Version 3.2 image analysis system). In the preparation of composite, epoxy resin, EPON<sup>TM</sup> Resin 8281 (Bisphenol-A-(epichlorohydrin)) and Polyetheramine D230 (PEA D230) were used as a matrix and curing agent, respectively. The curing agent, PEA D230 (32 parts by weight), was added into 100 parts of EPON<sup>TM</sup> Resin 8281. As comparison, the as-synthesized AgNPs, commercial silver nanoparticles (AgNPs) and silver flakes (AgF) were used as conductive filler and were added into the resin at 6vol.%, based on our previous work [6]. The mixture of epoxy and silver filler were then stirred manually for approximately 10 minutes and sonicated for 30 minutes to facilitate dispersion of the fillers. After that, the curing agent was then added into the mixture, followed by stirring for another 10 minutes. In order to remove bubbles, the mixture was vacuumed for approximately 0.5 hours at room temperature. The thin film was then prepared by placing the mixture on a spin coater, running at 2200 rpm before it was cured in an oven at  $80^\circ\text{C}$  for 2 hours, followed by post-curing at  $125^\circ\text{C}$  for 3 hours. The morphology of the composite was observed by SEM (model ZEISS SUPRA<sup>TM</sup> 35VP) and the electrical property of the composite thin film was evaluated by LCR meter, respectively. Table 1 shows the description of the samples.

Table 1: Description of prepared samples

Samples	Description	Average particle size
0 vol.%	Unfilled epoxy	-
Syn-6vol.%	Epoxy composite filled as-synthesized silver nanoparticles	(50.1±9.6)
F6vol.%	Epoxy composite filled commercial silver flake particles	(7.1µm±3.2)
N6vol.%	Epoxy composite filled commercial nanoparticles	(56.6±13.6)

## Results and discussion

In this study, AgNPs were prepared by chemical reduction method. During the synthesis process, reductant ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ ) was directly reduced  $\text{Ag}^+$  to generate metallic Ag atoms. The produced Ag atoms then acted as nucleation centres and catalysed the reduction of the remaining metal ions present in the solution. The coalescence of atoms led to the formation of metal cluster, which are normally stabilized by ligands, surfactants, or polymers [2]. In this study, it is believed that ascorbic acid which acted as a surfactant was adsorbed onto the surface of the Ag atoms, and thus prevented the nanoparticles from agglomerating. At the beginning of the process, the newly reduced Ag atoms acted as nuclei of the nanoparticles. With further processing time, these nuclei grew continuously. Indication of the formation of AgNPs was observed by the solution colour change. During this process, the solution went through a number of colour changes from light

yellow→yellow→greenish, before it stabilised. These colour changes indicate the growth of the AgNPs. In this process, the reaction can be expressed as follows [7]:

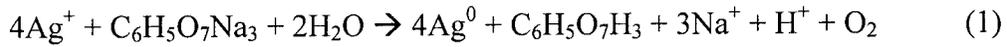


Figure 1(a) and (b) represent the TEM micrograph of the as-synthesized and commercial AgNPs, respectively. It is evident from Figure 1(a), that the as-synthesized AgNPs were quite uniform and mostly quasi-spherical in shape. Moreover, it can be noticed that the as-synthesized AgNPs were well dispersed with a low degree of agglomeration. In comparison, Figure 1(b) shows TEM image of the commercial AgNPs. From Figure 1(b), it was confirmed that the commercial AgNPs mostly existed in an irregular shape, with a mixture of spheres and short rod-like structure.

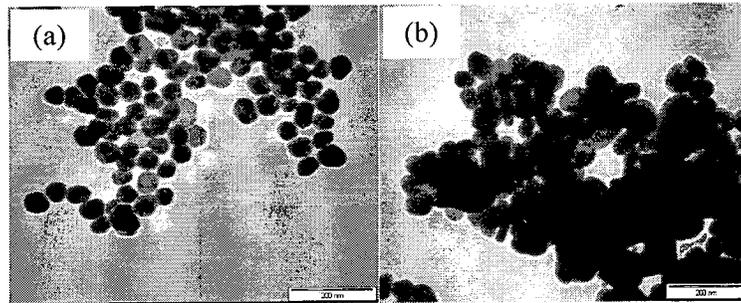


Figure 1: TEM micrograph of (a) as-synthesized AgNPs, (b) commercial AgNPs

Figure 2 shows the plotted X-ray diffractogram of the as-synthesized AgNPs. The obtained Bragg reflections index (111), (200), (220), and (311) which corresponds to the FCC structure also shows that the as-synthesized AgNPs were essentially crystalline. However, it can also be observed that the peaks are substantially broadened, indicating that the material is composed of very small silver crystallites. XRD patterns of nanoparticles exhibit several size-dependent features, leading to anomalous peak positions, heights, and widths. Previous work by Oliveira et al., [8] indicated that nano-sized metal particles are expected to present a lattice contraction due to high surface pressure, and a distinctive non-crystalline atomic arrangement.

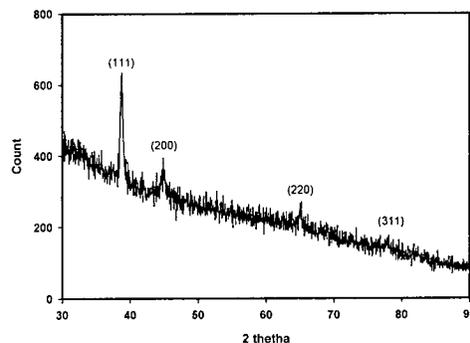


Figure 2: XRD pattern of as-synthesized AgNPs

Figure 3 (a) shows the plotted electrical conductivity of unfilled and filled thin film composite prepared at 6vol. % by as-synthesized AgNPs obtained from the present study with respect to commercial silver particles; e.g., AgNPs and AgF. As expected, the unfilled epoxy composite shows the lowest electrical conductivity ( $10^{-8}$  S/cm). In contrast, for the filled epoxy composite, the electrical conductivity was seem to increased seven fold from  $10^{-8}$  to  $10^{-1}$  S/cm. At this stage, the filled composite materials were believed to have changed its behaviour from insulator to conductor. The epoxy filled as-synthesized AgNPs showed the highest conductivity ( $10^{-1}$  S/cm) compared to

epoxy filled commercial silver AgNPs and AgF, even though it was prepared at a constant filler loading.

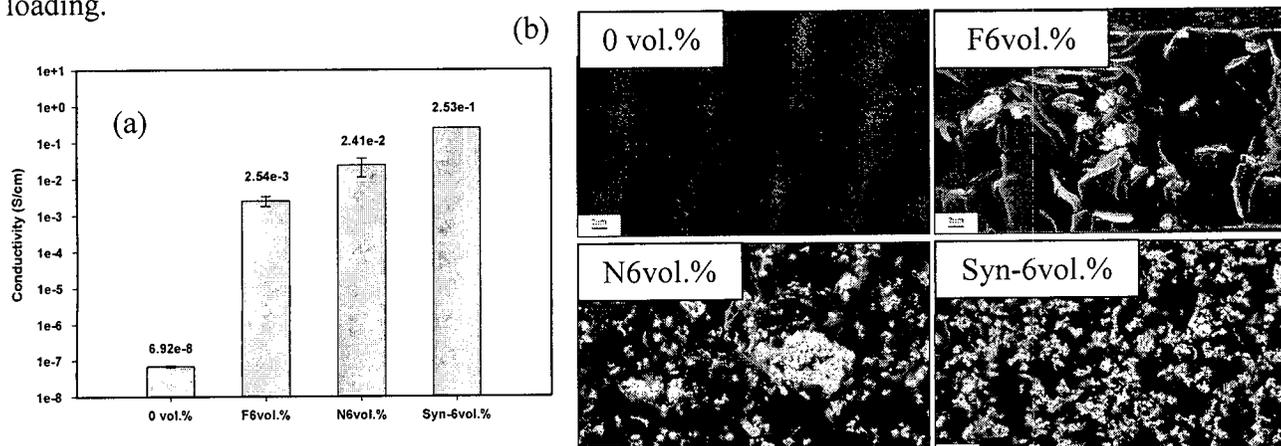


Figure 3: (a) Conductivity of silver filled epoxy thin film composites, (b) SEM micrograph of silver filled epoxy thin film composites

Theoretically, there are three situations are possible which is no contact, close proximity and physical contact between the conductive particles. However, electrical conduction only could be achieved mainly through physical contact and by close proximity of the conductive particles [9]. Electrical properties are directly dependent on the morphology of the silver nanoparticles embedded in the polymer matrix [10]. Thus, it should be noted that nano-sized silver particles which have better filler dispersion could also have close proximity due to their high surface area which enable electron to penetrate the thin gap ( $< 10$  nm) between the particles, hence reduce the percolation threshold compared to micron-sized silver. This observation can be supported by the SEM micrograph in Figure 3 (b). Additionally, compared to commercial AgNPs (N6vol.%), it can be suggested that better filler distribution represented by the as-synthesized AgNPs (Syn-6vol.%) could contribute to better filler dispersion throughout the epoxy matrix. This subsequently contributes to better current transfer, which leads to an improved conductivity property.

## Conclusion

Fine dispersion and narrow size distribution of the silver nanoparticles can be acquired by a simple, and partly green chemical reduction method. It was believed that ascorbic acid played a significant role in dispersing the particles, whilst lowering the degree of particle agglomeration. Formulated ECA with better particle distribution of the as-synthesized AgNPs showed a remarkable improvement in electrical conductivity as compared to commercial AgF and AgNPs.

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