

# Synthesis of silver nano-particles by EB irradiation

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**ABSTRACT** A new electron beam method has been successfully developed to prepare silver nano-particles at room temperature and ambient pressure, without any kind of catalysts. The structure, morphology, size, optical properties and the melting point have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), ultraviolet-visible spectrophotometer (UV-vis) and differential scanning calorimeter (DSC) were utilized to characterize the product. TEM results show that the average size of silver nano-particles is about 30nm in agreement with the calculated value size from XRD using Scherer formula.

**KEYWORDS** Silver nano-particle, Electron beam, Radiation, Electron accelerator

**CLC** O614.2, O572.2, O644.22, TF125.2<sup>+</sup>3, TH742

## 1 Introduction

Nano-particles of noble metals have been a subject of intense research due to their potential applications in microelectronics, and their novel optical, electronic and catalytic properties<sup>[1,2]</sup>. Ultra fine metal powder of silver is used as solder, dental fillings, circuit's boards, high-speed photographic film and a host of other applications<sup>[3]</sup>. Colloidal silver has a long history in medicine as a natural antibiotics. It is very effective in killing bacteria, fungi, parasites and cancer cells as well. However, viruses appear to be killed only when the size of the colloids is very small<sup>[4]</sup>. There are numerous publications on synthesis of Ag nano-particles in various glasses for non-linear optical applications<sup>[5]</sup>.

There are various kinds of method to prepare silver nano-particles, such as sol-gel processes, ion implantation, plasma arcing, sputtering on glass or polymers matrix, micro emulsion, radiolytic synthesis, etc. Among these preparation methods, the radiolytic synthesis of nanocrystals from metal ions in solution can provide a wide variety of mono-and multi-metallic systems with different structures<sup>[6]</sup>. However, applications of using electron beams as irradiation source to synthesize nano-particles in an aqueous solution, especially with the high-energy industry electron accelerator, are rarely reported in the literatures.

In this paper, we present a detailed study on synthesis, characterization of nanoparticles with silver nanoparticles for an example.

## 2 Experimental

All the chemicals used in this work are of analytical grade without further purification. They include AgNO<sub>3</sub>, polyvinyl alcohol (PVA) and isopropyl alcohol (IPA). Distilled water was used in the experiment. Solutions were prepared by dissolving certain amount of silver nitrate in the water. PVA was added to control the size of nano-particles and, moreover, to prevent aggregation of the nano-particles. IPA was added in appropriate proportions in the solution to act as scavenger of oxidative radicals (OH<sup>•</sup>). The solution should be prepared in a dark room to avoid the photodecomposition of silver nitrate. Then the solution was irradiated to different absorbed doses by 300keV 1mA electron beam from an EB facility at SU.

After irradiation, color change of the solution could be observed, from colourless before the irradiation to black after the irradiation, as the radiation induced silver nano-particles suspended in the solution. The suspended silver nano-particles were treated by 98% n-dodecanethiol (C<sub>12</sub>H<sub>25</sub>SH), which passivates, electronically and chemically, surfaces of the nanocrystal and nano-particles<sup>[7]</sup>. The treated solutions were kept for several hours to allow precipitation of

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the silver nano-particles. The silver precipitations were centrifuged. All the residual PVA and  $C_{12}H_{25}SH$  were removed by washing several times with ethyl alcohol (99.7%, density 0.79g/mL) until no suspended materials could be found on the surface when the solution was pored off. After vacuum dry at 60°C for 10hours, black silver nano-particle powders were obtained.

X-ray diffraction (Cu  $K\alpha$ ) was used to measure the particle structure. Visible absorption spectra of the silver nano-particles were recorded by a UV-visible spectrophotometer (Model DMS 100S). Morphology and particle size of the particles were determined by a transmission electron microscopy (Hitachi Model H-800), which was operated at 200kV of accelerating voltage. An NETZSCH STA 409 PG/PC differential scanning calorimeter (DSC) was used to check melting point of the silver nano-particles.

### 3 Results and discussion

Typical XRD result of the silver nano-particles is given in Fig.1. The XRD peaks at  $2\theta=38.38$ , 44.44, 64.70 and 77.72 degrees correspond to plane reflection of (110), (111), (220) and (311), respectively. All peaks were indexed as pure silver atoms in ASTM powder diffraction card No 4—783. The black powder is formed by silver atoms.

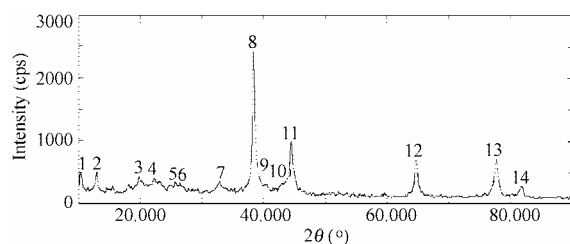


Fig.1 XRD pattern of nano-silver by the electron beam

Average size of the particles can be calculated by Scherer formula,

$$L=0.9\gamma/B(\cos\theta) \quad (1)$$

Where  $\theta$  is the diffraction angle,  $\gamma$  is wave length of the X-ray, and  $B$  is correlated to the diffraction peak,  $B=(\beta_{\text{sample}}^2-\beta_{\text{reference}}^2)^{1/2}$ ,  $\beta$  is the full width at the half maximum (FWHM) of the peak.

For peak 8 of  $2\theta=38.38$  in Fig.1,  $\beta_{\text{reference}}$  is 0.210 degrees and  $\beta_{\text{sample}}$  is 0.353 degrees, then average size

of the silver nano-particles is about 28.6nm. The calculated particle size is in agreement with the result of TEM observation, which will be discussed later.

UV-visible spectrophotometer was used to study dispersibility of the silver nano-particles in different solvents. An ultrasonic device vibrated the silver nano-particles to help dissolution them in different solvents. UV-VIS absorption spectra of the silver nano-particles dispersed in different solvents were shown in the Fig.2.

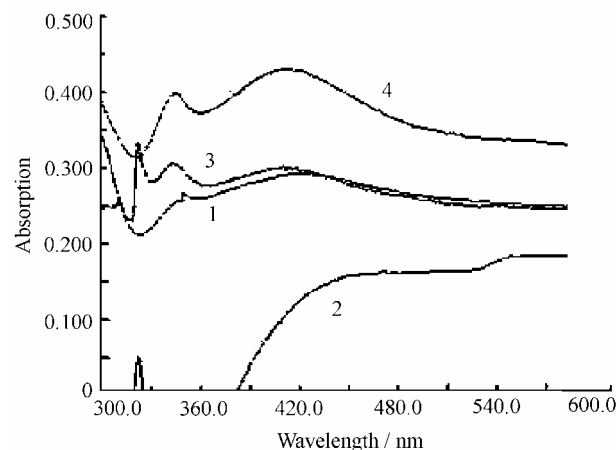


Fig.2 UV-VIS absorption spectra of silver nano-particles dispersed in different solvents. 1, chloroform 2, distilled water 3, acetone 4, ethanol

From Fig.2, one can see that the absorption peaks are different from each other for silver nano-particles in different solvents. The main absorption wavelengths are at about 340nm and 410nm. The two absorption peaks of the spectra may be explained by the fact that the particle sizes are different.

Typical TEM micrographs of the silver particles are shown in Fig.3 and Fig.4. The silver particles dispersed in different solvents have various aggregated morphologies. Dispersibility of the silver particles in chloroform was better than in other solvents. Similar experimental results have been reported by other groups<sup>[8]</sup>. The strong interactions between the silver nano-particles and chloroform could make silver particles well dispersed in chloroform. It is possible, therefore, to prepare polymeric nano-composites by means of solution mixing using chloroform as solvent.

The silver nano-particle sample used for TEM observation had been used for the XRD measurement. We found an interesting phenomenon that some particles looked like apparently severed, but actually they

were connected to each other, as shown in Fig.5.

served with other nano-particle materials.



**Fig.3** TEM micrographs of silver nano-particles dispersed in ethanol

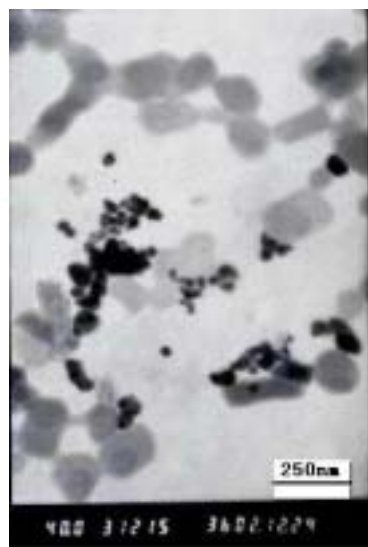


**Fig.5** TEM image of silver nano-particles in chloroform. The particles had been used to do the XRD

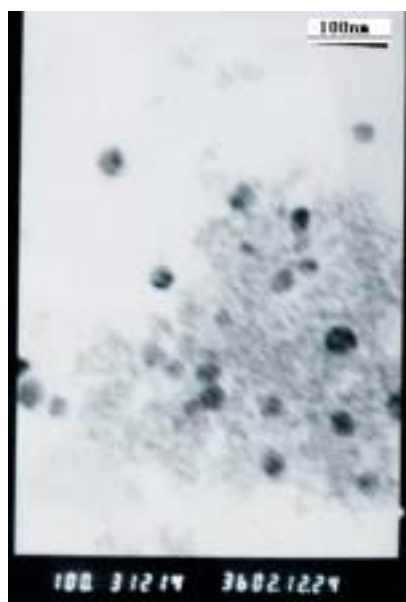


**Fig.4** TEM micrographs of silver nanoparticles dispersed in chloroform



**Fig.6** Electron diffraction pattern of the nano-particles

By the TEM observation, however, it seemed that the silver nano-particles began aggregating gradually after the X-ray irradiation. This suggests that melting point of the silver nano-particles is lower than normal. DSC measurement was performed to check melting point of the silver nano-particles. As shown in Fig.7, melting point of the silver nano-particles is about 128.5°C, far less than 961.6 °C, the normal melting point of silver. When particle sizes are in nanometer scale, their physical properties can differ greatly from the bulk materials. Lowered melting points can be ob-

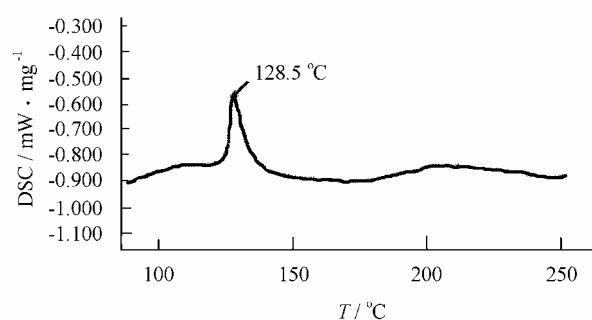
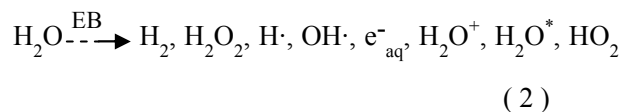


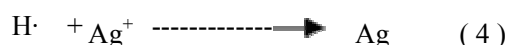
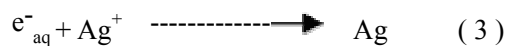
**Fig.7** DSC spectra of the nanoparticles (heating rate 10 °C/min)

Electron beams produce silver nano-particle as a

result of silver ion reduction by hydrated electron formed in solutions under electron beam irradiation, as described by Eq.(2)<sup>[9]</sup>.



As a hydrated electron has a standard electrochemical potential of  $-2.77\text{V}$  and the standard potential ( $E^\circ$  of  $\text{Ag}^+/\text{Ag}$ ) is  $+0.80\text{V}$ , the reduction of silver ions can occur with the following reactions.



#### 4 Conclusion

The following conclusions can be drawn from the experimental study.

(i) Silver nano-particles were prepared, without any kind of catalysts, at room temperature and ambient pressure, by electron beam irradiation of  $\text{AgNO}_3$  solutions with isopropyl alcohol as scavengers of oxidative radicals.

(ii) Melting point of the silver nano-particles is much lower than bulk silver.

(iii) Strong interactions between the silver nano-particles and chloroform could make silver par-

ticles disperse well in chloroform.

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**摘要** 在水溶液中, 常温常压下不加入任何催化剂, 用电子加速器辐照作为一种新的方法可以成功制备出纳米银。我们利用 XRD、TEM、UV、DSC 来分别表征材料的结构、形貌、大小、光学特性以及材料的熔点。

TEM 图像证明颗粒大小为 30nm, 这与 XRD 实验通过 Scherer 理论公式计算的结果相一致。

**关键词** 纳米银, 电子束, 辐照, 电子加速器,

中图分类号 O614.2, O572.2, O644.22, TF125.2<sup>+</sup>3, TH742