

## Preparation of silver nanoparticles on sol-gel base and study of their physical and morphological properties

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(Received: 15/5/2010, in revised form: 28/8/2010)

**Abstract:** In this study, we propose a simple approach to prepare silver nanoparticles. The silver nanoparticles were synthesized by chemical reduction of  $\text{AgNO}_3$  in the presence of tetrabutyl titanate ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ; TNBT) and metallic tin powder as reducing agent in water at room temperature. The structure and average grain size of prepared particles were characterized by transmission electron microscope (TEM), X-ray powder diffraction (XRD) and scanning electron microscope (SEM). Based on proposed method, nearly spherical shape nanoparticles with a mean diameter of  $17 \pm 0.6$  nm were obtained. The silver nanoparticles dispersed in tetrahydrofuran-dimethylformamide (THF-DMF) (1:1) mixture exhibit a broad UV-visible band.

**Keywords:** Silver nanoparticles synthesis; tetrabutyl titanate; Chemical reduction.

### Introduction

Numerous applications of metallic nanoparticles have resulted in high attention in preparation of these substances, recently. They are characterised by their potential physical and chemical properties, which make them highly applicable in optoelectronics, information storage, catalysis, biological labelling, photonics, photography and production of batteries [1–3].

In addition to traditional methods of their production new methods have also been developed. Among various metal nanoparticles, silver nanoparticles have been widely investigated because of their unusual property exhibition raised due to their size and shape which brings a variety of possibilities with respect to the technical applications. Silver nanoparticles have been produced using different electrochemical methods [4–7], thermal decomposition [8], laser ablation [9], microwave irradiation [10] and Chemical reduction of silver ions in the presence of sol-gel. A key issue among these techniques is the control of particle size, which is very important in various applications. Implementation of some

techniques is not cost effective and therefore, most researchers focus on the chemical reduction method because of its low cost and ease of operating apparatus [11, 12].

In this study, silver nanoparticles were synthesized by chemical reduction of  $\text{AgNO}_3$  in the presence of tetrabutyl titanate ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ; TNBT) as a stabilizing agent and metallic tin powder as a reduction agent at room temperature. The structure and the nature of the resulted particles were characterized using analytical methods including transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). The produced silver particles present a compact size distribution with a mean diameter of  $17 \pm 0.6$  nm.

### Material and procedure of nanoparticles preparation

Silver nitrate (Aldrich Co.) was used without further purification. Metallic tin powder, THF, DMF and tetrabutyl titanate (Merck) were also used without any purification. Double distilled water was applied during sample preparation.

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Nanosized crystalline silver nanoparticle was produced by chemical reaction method. Designated amounts of TNBT were gradually added to 0.22 g metallic tin powder. The mixture was then added with a solution of 70 ml silver nitrate (1M) and was stirred up for 10 minutes followed by a 6 hour resting time. Finally powders were dried at room temperature about 24 hours and washed with distilled water and filtered.

### Equipments

Silver nanoparticles were characterized using Philips CM 200 transmission electron microscopy by placing a drop of the particles in THF onto a carbon film supported on a copper grid. Elemental analysis was obtained using energy dispersive X-ray spectrometer (EDXS). The powder X-ray diffraction (XRD) patterns obtained on a XPERT-

Philips, using Cu K $\alpha$  radiation, were used for the identification of the any phase present and their crystallite size. Atomic absorption measurements were carried out with a Beckman DU 640 spectrometer. The surface morphology of the films was examined by a Philips-BAL-TEC scanning electron microscopy.

### Results and discussion

The crystallinity of silver nanoparticles was assessed according to their XRD patterns. Figure 1 shows the XRD patterns corresponding to Ag nanoparticles prepared (A) with and (B) without TNBT. As shown, (Figure 1A) three peaks are recognizable at

Bragg angles of 38.10, 44.33, and 64.42, respectively. Comparison of these data with those deduced for the powder diffraction of Ag (File No.87-0597) show that these peaks correspond to the (111), (200), and (220) planes of silver and indicates silver nanoparticles formation with cubic structure [space group: Fm3m (2 2 5)] and a lattice parameter of 4.086 Å. Furthermore, reflected peaks from (220) and (400) planes of TNBT overlap with reflected (200) and (220) peaks of Ag nanoparticles with slight shift to lower angles. The signals overlapping causes shape complexity of Ag nanoparticles peaks. But in the absence of TNBT, this complexity is not observed (see Figure 1B). The reflections of residual Sn powder can also be observed on both patterns. However, no trace of an Ag or Sn oxide phases were detected. The crystallite sizes of the two products were calculated by substituting the full width at half maximum (FWHM) and Bragge angles in Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

in which D corresponds to the mean crystallite in Å,  $\lambda=1.54$  Å is the X-ray wavelength,  $\beta$  corresponds to FWHM in radian and  $\theta$  half diffraction angle. By considering Eq. (1), it is found that the crystallite size of Ag in the presence of TNBT (22 nm) is smaller than that in the absence of TNBT (43 nm).

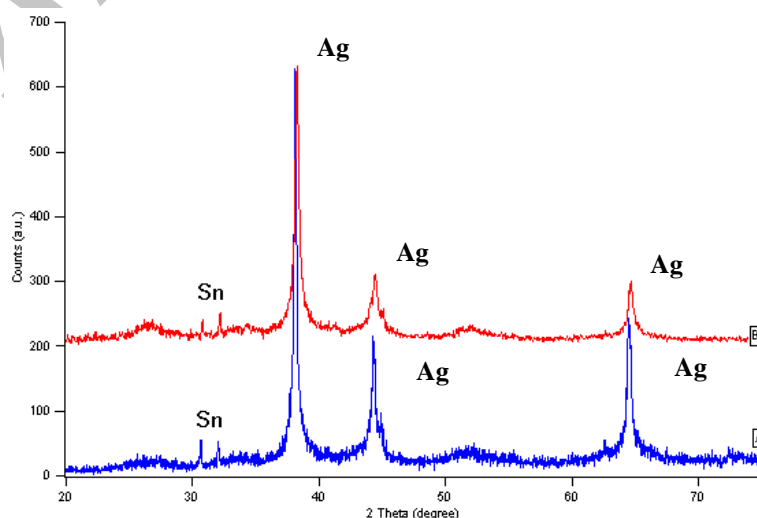


Fig. 1. XRD patterns corresponding to Ag nanoparticles prepared (A) with and (B) without TNBT.

A TEM image of resulted Ag nanoparticles in the presence of TNBT is shown in figure 2. It can be seen that the particles are spherical in shape. Analyzing a population of hundred particles from a portion of the grid indicates that the mean particle size is  $17 \pm 0.6$  nm. Fig. 3 presents EDX spectrum of the analyzed particles. Silver shapes the dominating signal. Certain amount of copper and carbon from the used grid holding nanoparticles is present. Ti peak suggests that the nanoparticles form in the TNBT matrix. A negligible quantity of Sn is visible. Scanning electron microscopy (SEM) embodies a highly professional capability for the observation and analysis of a broad range of surfaces. The SEM image of the nanoparticles in the presence of TNBT is shown in Fig. 4. The image shows that the size and distribution of silver crystallite are not uniform. Analysis of the micrographs of the sample show that the mean size of them is of the order of  $19 \pm 2$  nm which is in good agreement with TEM and XRD results.

The optical absorbances of as-prepared

and after 6 months sustained of nanoparticles in THF-DMF (1:1) mixture are shown in figure 5A and 5B respectively. The as-prepared sample (Fig. 5A) shows a dipole plasmon resonance band at 398 nm and indicates that the metal silver is formed using above mentioned chemical reduction reaction. The formation of the peak in this position attributed to excessive amount of silver to tin in the sample. The spectra begins with a broad absorption band as a plateau located at 200-280 nm and other absorption band as a shoulder appeared at around 300 nm that belong to hexadeca and octapoles resonances can be described well by Maxwell-Garnett model [13]. The surface plasmon peak position could be seen (Fig. 5B) to be red-shifted with increase in particles size due to quadrupole resonance and begins to emerge where the dipole resonance occurred [14]. It can be seen that the plasmon band shifts to higher wavelength and vanishes after 6 months due to significant aggregation.

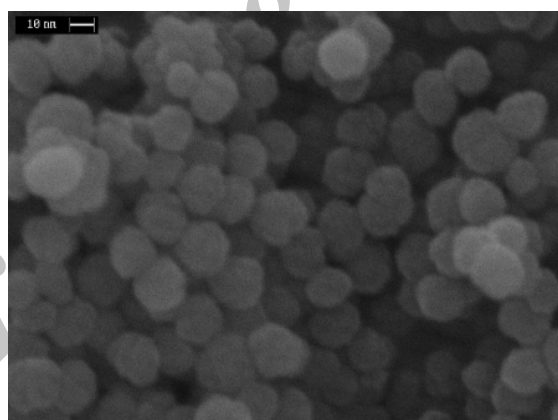


Fig. 2. TEM image of Ag nanoparticles in the presence of TNBT

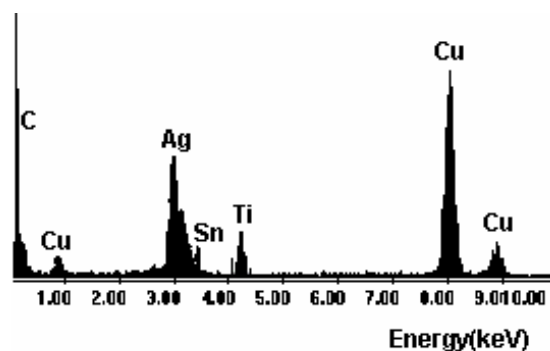


Fig. 3. The recorded EDS analysis from the Ag particles in the presence of TNBT

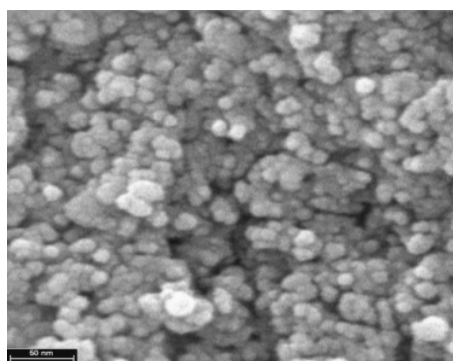


Fig. 4. SEM images of silver nanoparticles in the presence of TNBT

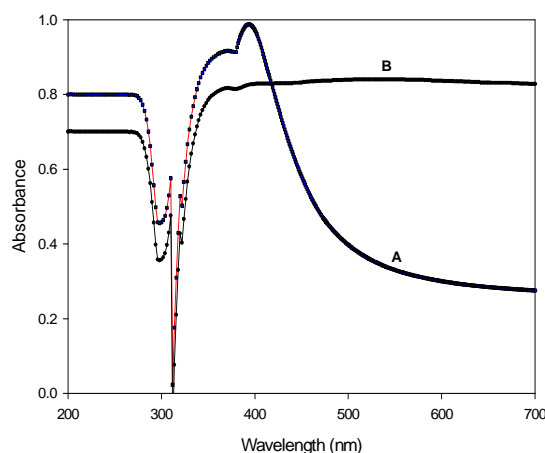


Fig. 5. UV-visible absorption spectra of as-prepared (A) and after 6 months sustained (B) of colloidal silver nanoparticles with TNBT in THF-DMF (1:1) mixture.

### Conclusion

Silver nanoparticles were prepared by a simple solution phase chemical reduction reaction of  $\text{AgNO}_3$  aided with  $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ -activated metallic tin powder in water at room temperature. Based on proposed method, nearly spherical shape nanoparticles have been formed. X-ray powder diffraction patterns of these particles shows the cubic structure of Ag metal. The particle size of silver particles in the as-synthesized material is  $17 \pm 0.6$  nm

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