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Correlation of Silver Size Nanoparticles Between TEM and QELS

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ABSTRACT

In this work, silver nanoparticles were synthesized by two methods: polyol and chemical reduction using sodium borohydride ($NaBH_4$). In both cases, silver nitrate was employed as starting metallic salt and Poly-vinyl pyrrolidone (PVP) as surfactant agent. The average nanoparticles size was correlated by transmission electron microscopy (TEM) and quasielastic light scattering (QELS). The experimental results indicate that the average particle sizes measured by QELS were slightly higher than those obtained directly by TEM. Therefore, this work confirms that the QELS technique can give rapid and approximate average-particle size values in comparison with those obtained through TEM direct observations.

Keywords: Ag, chemical synthesis, transmission electron microscopy (TEM), nanoscale, nanostructure.

INTRODUCTION

In recent years, synthesis and stabilization of nanoparticles has been subject to active investigation using different reducing agents. The physical and chemical properties of silver nanoparticles are promising for applications in catalysis, sensors, photoelectronics, and biomedicine [1]. Nanoparticles are defined as atomic arrangements with nanometric dimensions and usually with a small number of constituent atoms. Particles in the nano-regime are of immense importance due to their potential applications in different fields. The control of the size and the dispersion of nanometric metal particles have an important effect on their physical properties [2, 3]. Therefore, the synthesis and characterization of silver nanoparticles have attracted considerable attention from a fundamental and practical point of view. In particular, silver nanoparticles have received great interests due to their attractive catalytic, antibacterial, magnetic, and optical properties and potential applications in the fields of physics, chemistry, biology, medicine, and materials science and their different interdisciplinary fields [4, 5]. Silver nanoparticles have been obtained recently using different synthesis methods [6-8]. However, the chemical methods are reliable, simple to carry out, and available to control de size and shape of the small particles On the other hand, the structural determination of the nanoparticles becomes an important task to understand some of their properties [9-12]. In this scope, the use of the TEM and associated methods has been established as one of the main tools in the study of nanomaterials [13]. However, TEM characterization is usually slow, so that the use of

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new techniques in the measurement of average particle size and particle size distribution should be explored for a lot of studies in the laboratory at nanoscale regime.
In this investigation we report the experimental results on the synthesis and characterization of silver nanoparticles using a polyol method and the borohydride reduction ($NaBH_4$) method [11, 12]. The nanoparticles have been characterized by using high resolution electron microscopy (HREM) and QELS. The variations of particles size and distribution are evaluated through both techniques.

EXPERIMENTAL DETAILS

Silver nanoparticles were synthesized following polyol method [11] and the reducing agent sodium borohydride [12]. Analytically pure $Ag(NO)_3$, poly-vinyl pirrolidone (PVP) and ethylene glycol (EG) were used as the starting materials. In the case of polyol method; vials with 9 ml of ethylene glycol were placed in an oil- bath of silicone. A poly-vinyl pirrolidone 1 M (PVP) solution in ethylene glycol was added. The mixture was magnetic stirring (150 rpm) and heated at 150°C. To reduce the Ag ions from sodium borohydride reducing agent, an aqueous solutions of $NaBH_4$ (0.2 M) were added drop wise to the PVP containing metal ion mixtures at room temperature. 0.2. 0.1 and 0.05 M of Ag concentrations were prepared. The structural and morphological characteristics of the dispersed metallic nanoparticles have been studied using a Philips Tecnai F20 transmission electron microscope with a field emission gun attachment and dot to dot direct maximum resolution of 0.23 nm. TEM specimens were prepared by dispersing and subsequent drying a drop of colloidal solution on a copper grid (3 mm in diameter) covered with an amorphous carbon film. The average particle size and the distribution of particle size were measured using QELS Brookhaven equipment (90 Plus). All samples were previously dispersed using ordinary ultrasound equipment.

RESULTS AND DISCUSSIONS

Figure 1 shows UV–Vis absorption spectra of silver nanoparticles after chemical synthesis. The curve indicates a characteristic peak of surface plasmon resonance of approximately 400 nm, which indicates the formation of silver nanoparticles [14]. The value of the UV-Vis absorbance peak was between 380 and 430 nm. The color of the solution was dark brown in the case of nanoparticles reduced with $NaBH_4$ and dark green in the case of small particles produced by ethylene glycol.

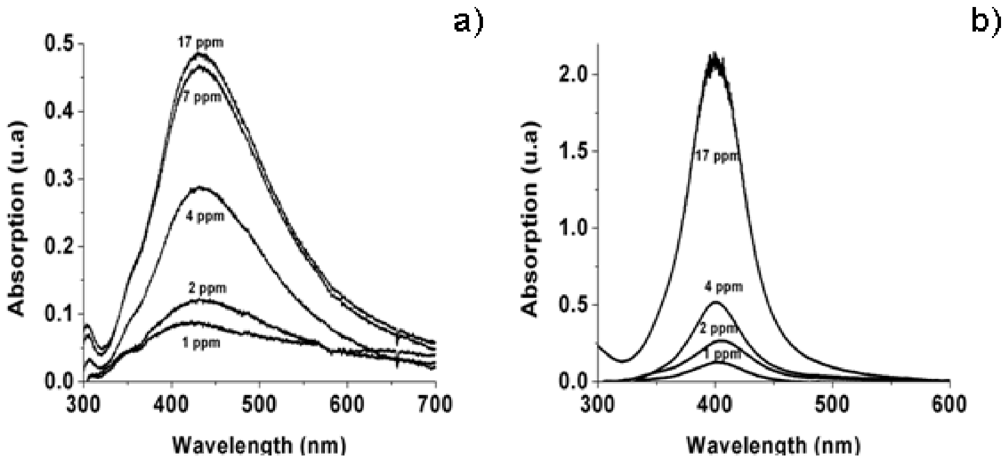

Figure1. UV-Vis spectra of samples a) reducing with EG, b) reducing with $NaHB_4$

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With decreasing the concentration of nanoparticles, decreases the intensity of the characteristic energy band and also the plasmon peak tends to shorter wavelengths resulting in smaller particle sizes. It has been reported that as surface plasmon peak is located toward longer wavelengths when particle sizes are larger [14-16].

Figure 2a shows a low magnification transmission electron microscopy (TEM) image of Ag particles using EG as a reducing agent. The morphology of the particles is semi-spherical and the formation of agglomerates is not appreciated. Figure 2b show the chemical analysis generated by EDS. Only Ag signal from the sample have been observed (C appear from the support).

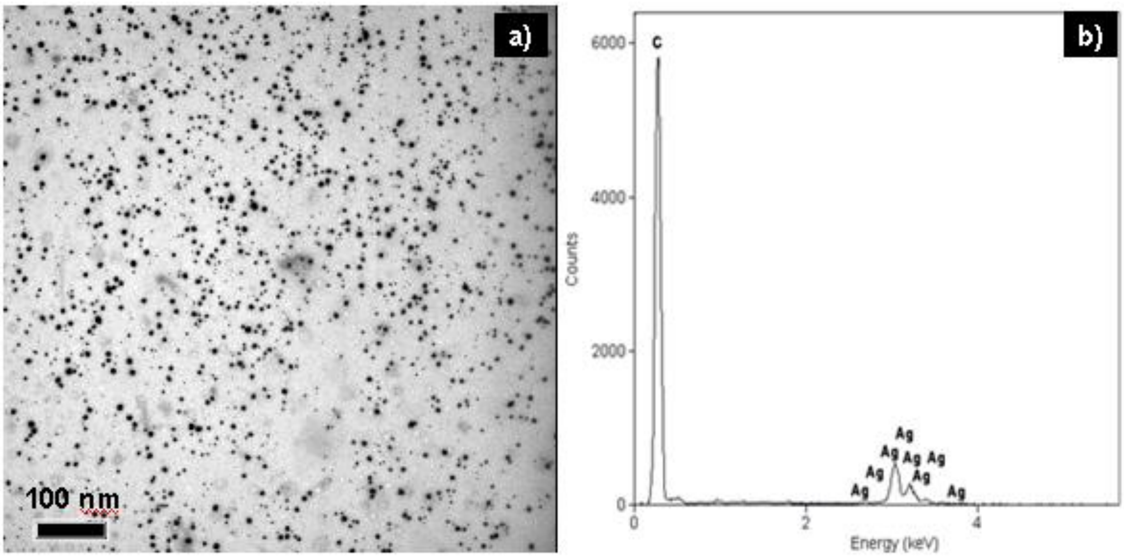

Figure 2. a) Low magnification TEM image of Ag nanoparticles synthesized by a polyol method, b) EDS chemical analysis of the nanoparticles produced.

In order to compare the particle size and the particle size distributions obtained in either TEM or QELS techniques, measurements in both types of specimens (produced by borohydride and polyol reducing agents) in the concentration of 0.2 M were carried out. The size of these nanoparticles can be measured directly from the TEM image. The sample population was 200 particles.

It can be seen that the average particle size was 63 nm. The particles have a wide particle size distribution as shown in figure 3a. It is interesting to note that even when the Ag sample reveals a larger distribution in particle size, there are still about 75% with about 63 nm of particle size of the sample. Figure 3b illustrates a typical graph of the average size and the particle size distribution after QELS analysis. The average particle size is about 76 nm which is greater that those obtained by TEM. Furthermore, the particle size distribution shows a bimodal behavior, however a high frequency of particles have an average particle size of about 75 nm.

Figures 4a-b shows low magnification transmission electron microscopy (TEM) images of Ag nanoparticles using $NaHB_4$ as a reducing agent. In the same way, the morphology of the particles tends to semi-spherical shape and it is no appreciate particles agglomeration. The particle size distributions obtained by TEM for Ag nanoparticles are illustrated in figure 5a, the average particle size is 39 nm, and the particle size distribution is greater than in the case of EG. Figure 5b shows the particle size distribution histogram for the QELS analysis. The average particle size of about 46 nm and similar size dispersion for this sample in comparison of EG is observed. In this sample, a high percent of particles were found between to 30 to 40 nm in size.

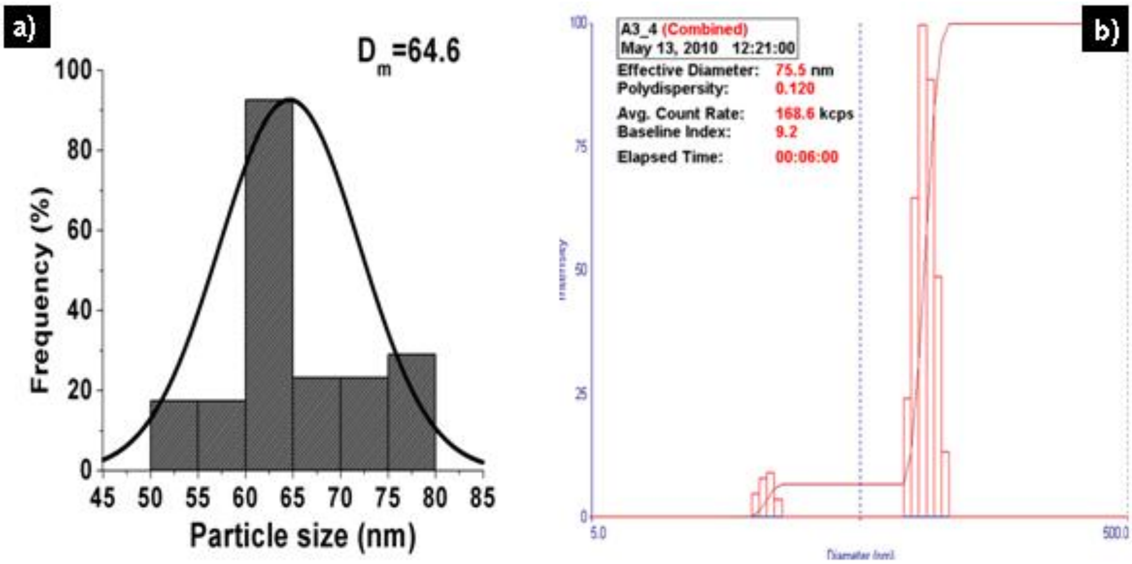

Figure 3. Average-particle size and size distribution of: a) histogram obtained directly by TEM observation and b) the histogram obtained by QELS technique.

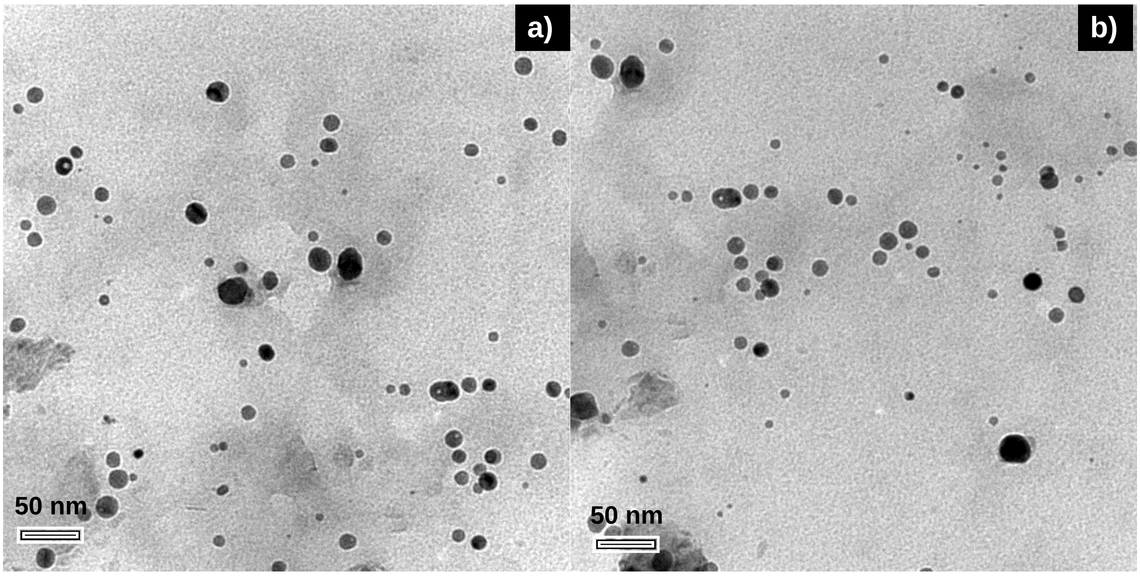

Figure 4. In a) and b) low magnification TEM images of Ag nanoparticles synthesized via $NaHB_4$ reducing agent in water.

In both types of samples (reducing with NaHB4 or EG) the values of the average particle size measurement through QELS, are indicated slightly higher values than that measure with directly by TEM observation. These results suggest that there is some uncertainty between the two methods, being more reliable, direct studies obtained by TEM. However, it is important to note that the results obtained by QELS are a very good approximation of the results obtained by TEM. In addition, QELS results will be more reliable as the dispersion of the particles is better.

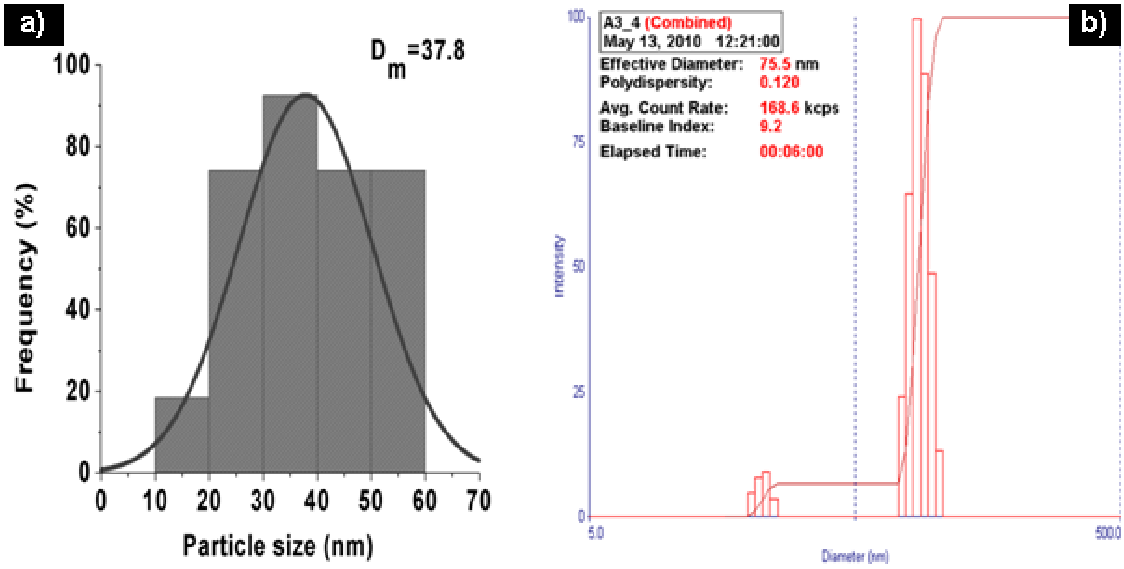

Figure 5. Average-particle size and dispersion of the a) histogram of particles measurement directly by TEM and b) the histogram obtained from QELS technique.

CONCLUSIONS

Silver nanoparticles of average size in the range of less than 100nm have been synthesized. The average particle size and the dispersion of the small particles have been evaluated through TEM and QELS techniques. The average-particle sizes values obtained by QELS were slightly higher than those obtained directly by TEM. However, the QELS values are a very good approximation of the TEM results. In addition, the average particle size obtained by QELS will be more reliable as the dispersion of the particles is better. Therefore, this work confirms that the QELS technique can give rapid and approximate average-particle size values in comparison with those obtained through TEM direct observations.

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