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Method of Receive a Nanoparticles of Noble Metals with Average Size Less Than 3 nm for LSPR Research

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Abstract: The paper presents a simple although effective method of obtaining gold and silver nanoparticles of average size of less than 3 nm. The nanoparticles were obtained by the Bredig's electric arc method. Then colloidal preparations were centrifuged with acceleration equals to 29000 xg. It has been showed that subjecting the colloid to the hour centrifugation process repeated four times allows to obtain nanoparticles whose size does not exceed 5 nm. The nanoparticles prepared using this method were characterized by a high purity that depended only on the water and the cleanliness of the noble metal wire which have been used. Furthermore, it was observed that the absence of conglomerates and joins of the particles is typical for transmission electron microscopy methods.

Keywords: Ag nanoparticles, Au nanoparticles, TEM, centrifugation nanoparticles.

1 Introduction

Production of nanoparticles, that are supposed to be used in biology, medicine, science and technology, using Bredig's electric arc method [Bredig G (1889)] is not common due to the fact that it is practically impossible to control the size of nanoparticles. On the other hand, this method, same as its modifications, is very cheap and simple namely it consists in fragmentation the metal in an electric arc. The most commonly used dispersion medium for metal fragmentized in electric arc is demineralized water, this from its purity both the stability and the quality of the colloid depends on. In this method, it was obtained nanoparticles the average size has a normal distribution with a large variance. In comparison to the currently available nanoparticle production methods, that use laser [Véron (2013); Bisker (2012)] chemical [Malina (2012); Xu (2007)] and many others [Sun (2014); Semenova (2014)] this seems to be the less popular. However, production by Bredig's method is advantageous in the case of fundamental research such as localized surface plasmon resonance [Sandu (2013); Scholl (2012)].

2 Experimental methods

TEM investigations were carried out on transmission electron microscopy Titan Cubed 80-300 at 300 kV. The centrifuge process of gold and silver colloids was carried out on the

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MPW 251. Colloidal preparations (date of production of silver 2011 and gold 2012) were purchased from NanoTech Poland Company. The specimens for the TEM observations were prepared by dropping the colloid drop on a carbon film supported on a 300 mesh copper grid. TEM studies were used to determine the nanoparticle size distribution. The grain size histograms were obtained by considering about 200 nanocrystals and approximating the shape of each nanocrystal by a sphere.

3 Results

Preparations of colloidal gold were poured into 12 test tubes with a capacity of 12 ml. The tubes with colloid were subsequently centrifuged with parameters: centrifugal acceleration-29000 xg, RPM-14000 for one hour. The extension of time resulted in significant heating of both: system and tubes with colloid, which resulted likely from the operation of the engine and friction associated with the presence of air in the chamber centrifugation. After this time, the tubes were opened and about 2/5 of their top capacity were taken. The tubes were refilled with colloidal gold and again subjected to centrifugation. This procedure was repeated several times until a sufficient amount of colloid that allows the division to the next fractions has been prepared. This process has been schematically shown in Figure 1. As a result of such carried out process 4 fractions colloid were obtained, on which research by transmission electron microscopy were conducted. The first fraction contained nanoparticles with sizes from 1 nm to several micrometers. Particles with the largest size have deposited on the bottom of the tube in the form of dense sediment. On Figure 2 an example of the particles collected from the top of the tube is shown. The histogram of the size is shown on Figure 3. The second fraction still contains large nanoparticles - Figure 4 histogram, but it the cut-off this above 80 nm might be noted. Third fraction (shown in Figure 5.) still contains nanoparticles size greater than 10 nm but their number has been significantly reduced. Last fourth fraction contains only nanoparticles with size less than 5 nm that is showed on Figure 7 and Figure 8.

Analogical studies have been conducted for colloidal silver. Centrifugation was performed according to the diagram the Figure 1. The four fractions have also been received. In Figure 9 the histogram of the size of silver nanoparticles is presented moreover Figure 10. shows the examples of particles. As in the case of colloids of gold, silver centrifuged from the first fraction contained particles from the size of nanometers to several micrometers. Also, here the largest particles have been deposited on the bottom of the tube. Histograms for the fractions 2 and 3, shown in Figure 11 and 12, do not show the difference between them, the particles in the size up to 25 nm are still observed. Only the last 4th fraction contains only particles below 5 nm. Histogram for this fraction was shown in Figure 13. In Figure 14 numerously occurring the silver nanoparticles with the sizes less than 5 nm have been presented. Summary of the study is presented in Table 1. There is a noticeable difference between the average sized nanoparticles of silver and gold amounting to 0.3 nm, which may be explained by their different specific weight. A significant advantage of this method is that obtained particles do not form the conglomerates, which was observed in the most of the works related to the nanoparticles in the TEM studies [Dell' Erba (2012); Saxena (2012)]. Conglomeration of nanoparticles makes it difficult to subject functionalization and impossible research such as plasmon resonance.

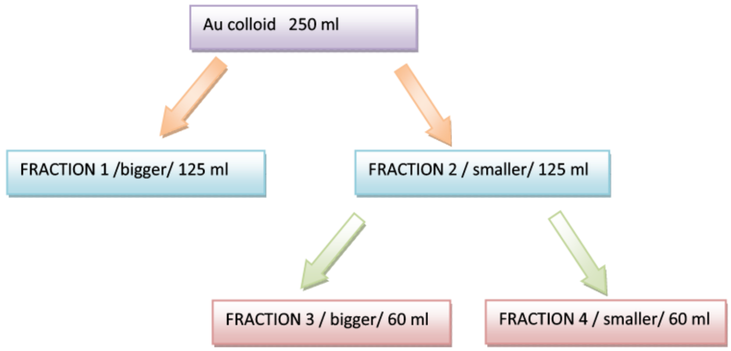

Figure 1: Schematic distribution of colloidal gold in the 4 fractions with a capacity values.

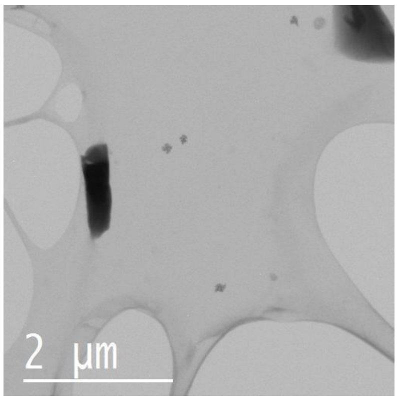

Figure 2: TEM micrograph of gold nanoparticles from the fraction 1

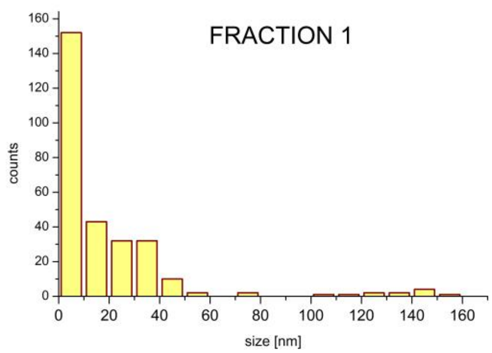

Figure 3: Histogram of the Au nanoparticle size made from fraction 1

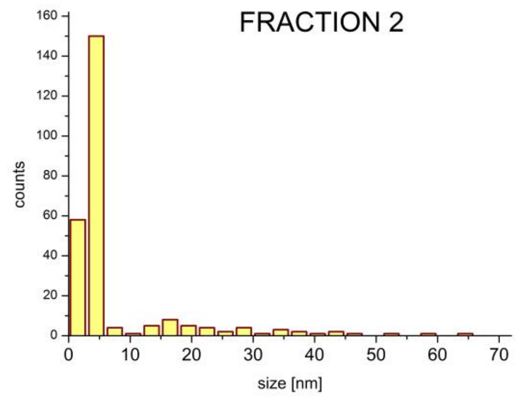

Figure 4: Histogram of the Au nanoparticle size made from fraction 2

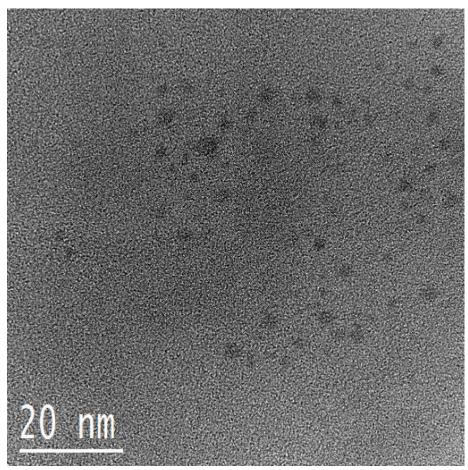

Figure 5: TEM micrograph of gold nanoparticles from fractions 3

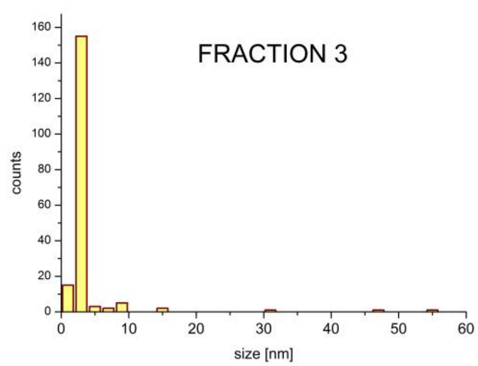

Figure 6: Histogram of the Au nanoparticle size made from fraction 3

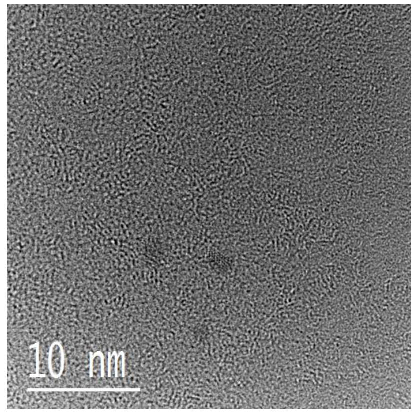

Figure 7: TEM micrograph of gold nanoparticles from fractions 4

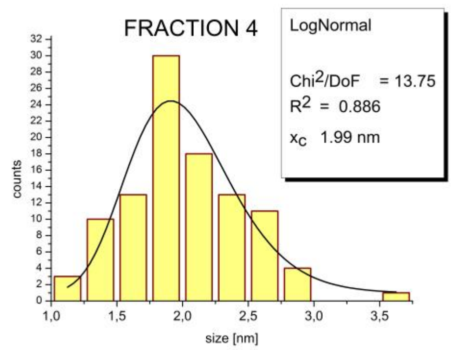

Figure 8: Histogram of the Au nanoparticle size made from fraction 4

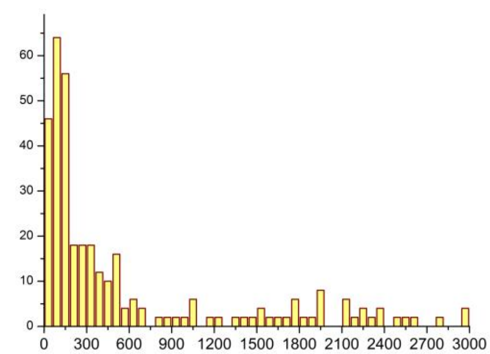

Figure 9: Histogram of the Ag nanoparticle size made from fraction 1

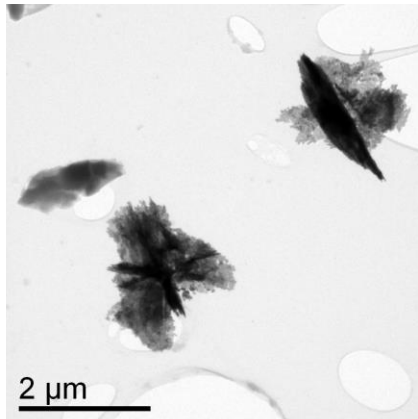

Figure 10: TEM micrograph of gold nanoparticles from fractions 3

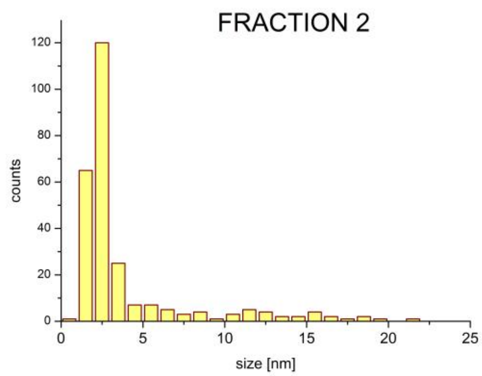

Figure 11: Histogram of the Ag nanoparticle size made from fraction 2

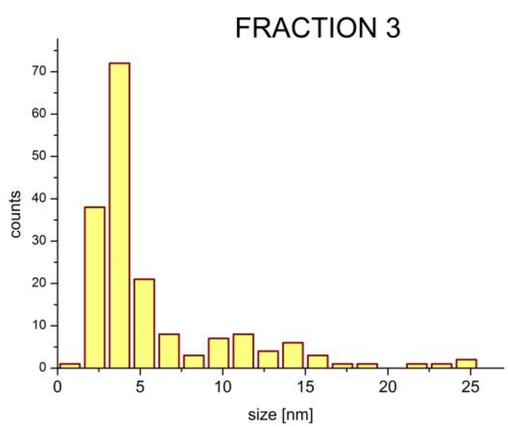

Figure 12: Histogram of the Ag nanoparticle size made from fraction 3

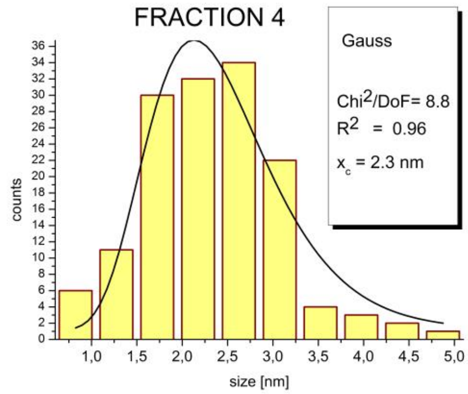

Figure 13: Histogram of the Ag nanoparticle size made from fraction 4

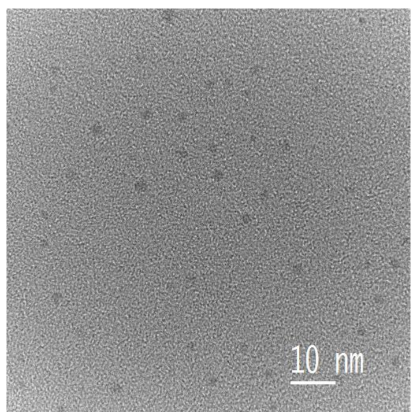

Figure14: TEM micrograph of gold nanoparticles from fractions 4

Table 1: Summary of the study

Fraction	Au	Ag
1	From 1 nm to few micrometers	From 1 nm to 3000 nm
2	From 1 nm to 70 nm	From 1 nm to 25 nm
3	From 1 to 10 nm Single particle sizes up to 55 nm	From 1 to 25 nm
4	From 1 nm to 4 nm Average size 2 nm	From 1 to 5 nm Average size 2,3 nm

4 Conclusion

The paper presents a simple method for the preparation of gold and silver nanoparticles with sizes less than 5 nm. Even though the method is cheap and simple it is unfortunately characterized by a long preparation process of such colloids. However, the obtained nanoparticles are characterized by high purity, which depends depending only on the water that was used. Author's experience shows that the colloid retains its parameters for at least six years. Biological or medical applications do not require such small particles whereas in basic research such as studies of the LSPR it is important to obtain a clean and particle with controlled size that is why this method seems to be the most suitable. The method is not only limited to the preparation of nanoparticles of a small size, it is also possible to collect particles from the bottom of the tube and obtain nanoparticles of intermediate size. The method presented in the work allowed to obtain silver nanoparticles with an average size equal to 2.3 nm and 2 nm gold.

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