

# A Study on the Oxygen Percent and the Crystalline Structure of Silver Nanoparticles Obtained by Electrochemical Method

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## ABSTRACT

In this paper silver nanoparticles (NPs) which are synthesized by a simple plasma arc discharge method, that is a kind of electrochemical methods, are examined. The method is very simple and silver NPs are obtained very fast by means of two polished silver plates and electrochemical cell. The effects of changing some terms of the experiment including using Hydrogen peroxide ( $H_2O_2$ ), temperature and the medium of experiment on oxygen percent and crystalline structure of silver NPs have been studied by transmission electron microscopy, UV-visible spectrophotometry, and X-ray diffraction. Water medium gets larger nanoparticles with less oxygen content compare to air medium. The size of synthesized nanoparticles become smaller and they also become more spherical by using  $H_2O_2$  in air medium. In water medium, the size and concentration of the silver crystallite increase by temperature growth and adding  $H_2O_2$  respectively.

**Keywords:** Silver; Nanoparticles;  $H_2O_2$ ; Electrochemical method.

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## 1. Introduction

Metal nanoparticles have often been studied and used in the different areas of nanotechnology<sup>[1, 2]</sup>. Nanoparticles (NPs) have a larger surface area than macro sized materials. Therefore they have distinct properties in comparison with the bulk form of the same materials. NPs are being used in the field of biosensors, biomedicine and also diagnosis, drug delivery and treatment for many diseases<sup>[3]</sup>.

A lot of studies carried out in the last three decades show that silver NPs have valuable properties namely unique optical properties associated with the Surface Plasmon Resonance (SPR), well developed surfaces, catalytic activity, high electrical double layer capacitance, etc. In particular, silver NPs are being used in the development of new generation of electronic, optical and sensor devices<sup>[4]</sup>.

It should be noted that the colloidal silver has attracted more attention because of different properties such as good conductivity, chemical stability, catalytic and antibacterial activity. Moreover, it has been shown that the growing small particles of silver are more effective catalysts than stable colloidal particles<sup>[5]</sup>. The reduction rate catalyzed by them could be noticeably faster than the stable and larger silver NPs which are the final products of growing particles. Overall, it can be said that the catalytic activity of silver NPs is dependent on their size<sup>[5]</sup>. Furthermore silver NPs are used for purification and quality management of air, coating for solar energy absorption, imaging, intercalation material for electrical batteries, as optical receptors, for bio labeling<sup>[6]</sup> and cancer treatment<sup>[7]</sup>.

A lot of methods have been tried to obtain silver NPs with various shapes and sizes, like photochemical method<sup>[8,3]</sup>, electron irradiation<sup>[9]</sup>, laser ablation<sup>[10]</sup>, microwave-assisted<sup>[11]</sup>, electrochemical and etc.

In most of these methods, the size of particles obtained cannot be controlled easily and because the process demands stabilizing agents and also lots of materials, is not simple. Particles obtained by the electrochemical methods have high purity and their size can be controlled easily without using expensive equipment. Among these methods, the

one that the current search is based on it<sup>[1]</sup>, results in long-lived silver particles without using stabilizing agents in the process of electrochemical. The method is very simple and there are not a lot of terms to adjust, so the effect of some terms of the experiment including i: using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ii: temperature and iii: reaction in water medium or in air medium on results were analyzed.

## 2. Experimental

### 2.1 Materials and Set up

The simple set up for the arc plasma method was used for producing silver NPs. The system was made up of two electrodes in two electrochemical cell medium (distilled water or air). The anode and the cathode were two polished silver plates (80mm ×10mm ×1mm) and they were vertically placed face to face, 10mm apart. It should be mentioned that the electrolysis performed at a constant voltage. In water medium, a magnetic stirrer was used for intensive stirring during the process of electrolysis to prevent the precipitates.

### 2.2 Methods and analysis

The products were analyzed after each experiment to check the effect of changing conditions on the products, as follow:

(1) At first experiment, the electrochemical cell was without water, the voltage was 22V which was turned off after 30 minutes. After that, the electrochemical cell was filled with 50ml distilled water. The solution was filtered by means of a 3µm filter paper (sample 1A) and then 3 drops of H<sub>2</sub>O<sub>2</sub> was added to the solution (sample 1B). Before adding H<sub>2</sub>O<sub>2</sub>, a gray solution obtained and after adding H<sub>2</sub>O<sub>2</sub>, the solution became so lucid and large particles in solution disappeared.

(2) In the second experiment, electrolysis was performed with 50ml distilled water in the temperature range 70-80 °C at the constant voltage of 22V. The polarity of the direct current was constant and the process continued for 30 minutes. After filtering (sample 2A) 3 drops of H<sub>2</sub>O<sub>2</sub> was added to the solution (sample 2B).

(3) The third experiment was done with 50ml distilled water in the room temperature at a constant voltage of 22V. In this sample H<sub>2</sub>O<sub>2</sub> was not used (sample3).

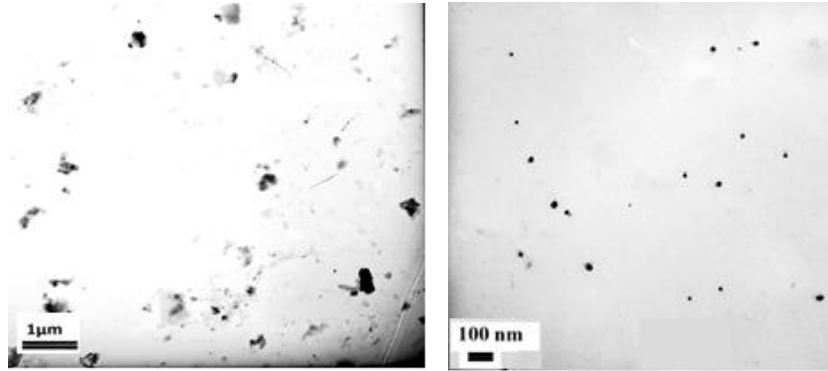
Finally the absorbance spectrum of the samples was measured by a Varian Cary-500 spectrophotometer at room temperature. The NPs crystal structure was measured by X-Ray Diffraction (XRD) (a STOE with Cu-Kα radiation). Transmission electron microscopy (TEM) (LEO-912-AB) with resolution 700KX and PhilipsEM 208(100 KV) with resolution 200 KX analysis was used to estimate the size and shape of the NPs in solution.

## 3. Results and discussion

The effect of temperature, using H<sub>2</sub>O<sub>2</sub> and some other terms on the size of silver NPs were studied in previous work<sup>[1]</sup>. In this paper, the main concern was to examine the effect of H<sub>2</sub>O<sub>2</sub>, temperature and experimental medium on the oxygen percent and crystallites of obtained silver NPs.

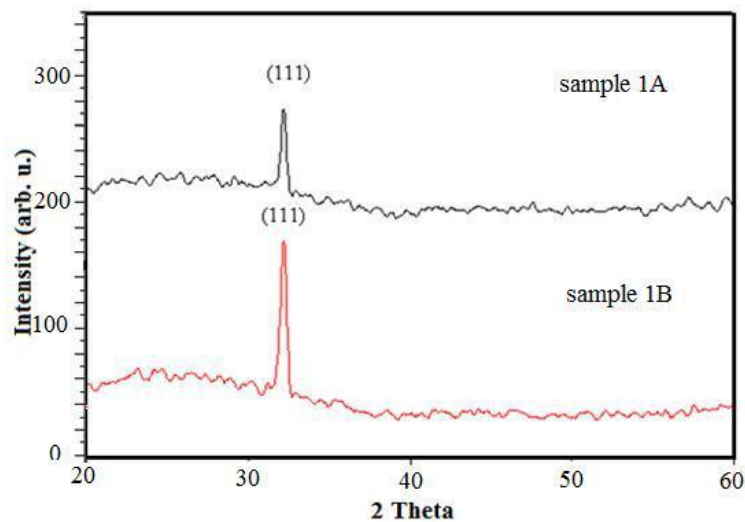
After the first experiment a very dark solution (sample 1A) which was containing a lot of micro- and nano-particles obtained. So it had to be filtered. After filtering, 3 drops of H<sub>2</sub>O<sub>2</sub> was added to the solution and the color of that changed to yellow immediately (sample 1B).

**Figure 1** shows the TEM images of nanoparticles of sample 1A and 1B .The size of NPs in sample 1A is about 230 nm and in sample 1B is about 25nm. It is obvious that in sample 1B by adding H<sub>2</sub>O<sub>2</sub> particles became smaller and spherical.



**Figure 1.** TEM image of sample 1A (left) and sample 1B (right).

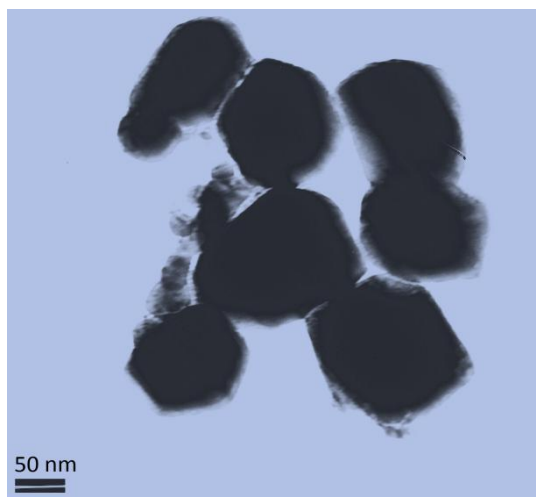
The optical density was measured immediately after the experiment and also one week later. Sample 1 doesn't show plasmon peak which indicates it doesn't behave as metal. According to optical density results of sample 1, nanoparticles have more absorbance on the day of doing the experiment, because they were distributed in all over the solution. After one week, the nanoparticles stick to each other and deposit.



**Figure 2.** XRD analyze of sample 1A (up) and sample 1B (down).

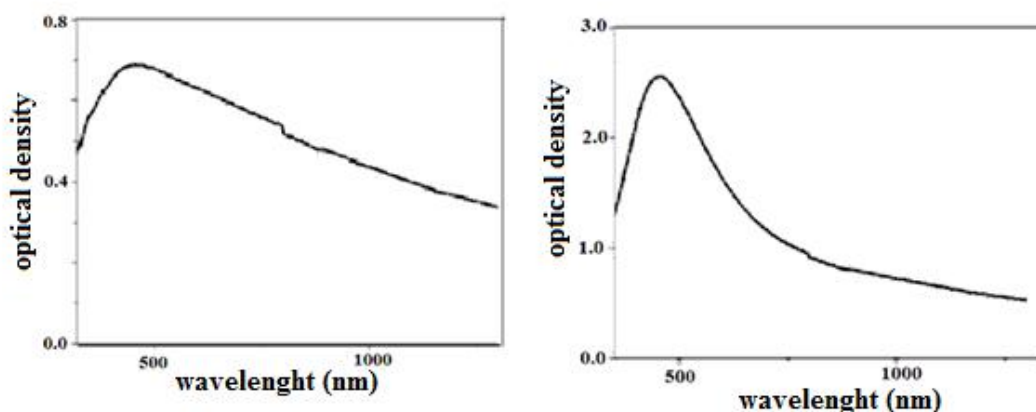
**Figure 2** shows XRD patterns of sample 1A and 1B. In this figure,  $\text{Ag}_2\text{O}$ (111) peak is clear<sup>[12, 13]</sup>. The average size of nanocrystals was estimated by the Scherrer equation. The average size of crystallite before adding  $\text{H}_2\text{O}_2$  have been calculated 30.6nm and after that 23nm. So XRD analysis results show that by adding  $\text{H}_2\text{O}_2$  the size of crystallite decreases. Before adding  $\text{H}_2\text{O}_2$ , the average size estimated by XRD patterns was smaller than what TEM images showed, but after adding  $\text{H}_2\text{O}_2$ , XRD results are in common with TEM images. These results show that by adding  $\text{H}_2\text{O}_2$ , nanoparticles nearly reduction to single crystallite. Increasing XRD peak intensity of sample 1B indicates the crystallite concentration increases in this sample.

According to the TEM analyze the average size of nanoparticles in sample 2B was about 102nm (Fig. 3). Black core and gray shell seen in this image indicate two compounds in the nanoparticles with two densities. Ag and  $\text{Ag}_x\text{O}$  make the core and the shell of this nanocomposite respectively.



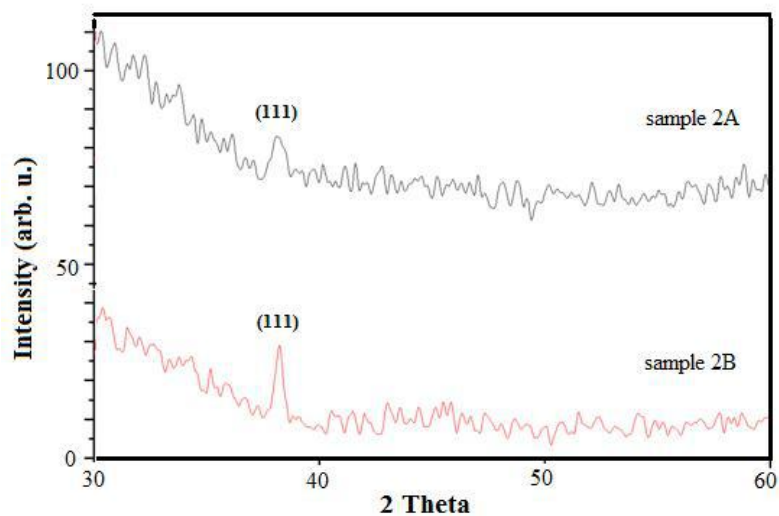
**Figure 3.** TEM image of sample 2B.

The optical density of sample 2A and 2B are presented in Figure 4. As it is shown in these curves, sample 2B plasmon peak is narrower and stronger than sample 2A, because the particles were sticking to each other and did not exist in all over the solution before adding  $H_2O_2$ , and adding  $H_2O_2$  caused smaller particles with uniform distribution. The plasmon peak of these samples appears at 450nm; peak position could be changed by increasing size, increasing geometrical anisotropy, decreasing the metallic character of nanoparticle<sup>[14]</sup>, then peak position of sample 2 influenced by with hexagonal shape of diameter 100nm and oxide shell.



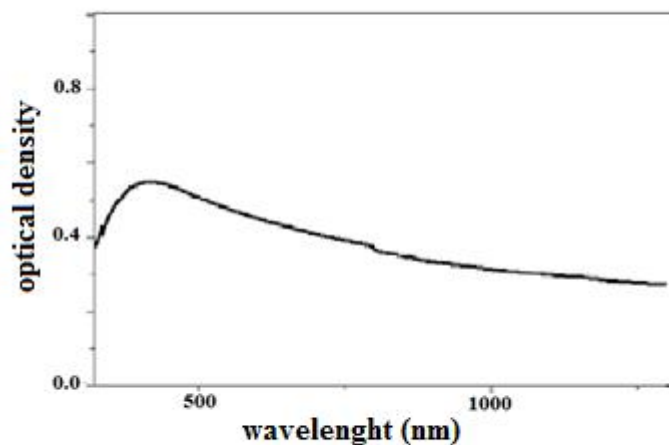
**Figure 4.** Optical density of sample 2A (left) and 2B (right).

**Figure 5** presents the XRD patterns of samples 2A and 2B, respectively. This fig. shows Ag(111) diffraction peak. More intensity of Ag(111) peak after adding  $H_2O_2$  deduces Ag crystallite concentration increase in solution which is indicated by increasing absorption by adding  $H_2O_2$  in fig. 4. Due to Scherrer equation, the size of crystallite calculated is about 25.8 nm.



**Figure 5.** XRD analyze sample2A (up) and 2B (down).

Sample 3 was a colloidal solution. It is obvious in Fig.6, that this solution has the least absorbance among all, because after synthesis, most of nanoparticles are aggregate and deposited.



**Figure 6.** Optical density of sample 3.

Figure7 presents XRD pattern of sample 3. This figure shows Ag(111) diffraction peak. The size of suspend nanoparticles, according to Scherrer equation was about 11.7nm. In sample 3, by decreasing the synthesis temperature, the Ag(111) diffraction peak width increased that confirms crystallite of silver decline, in every nanoparticle.

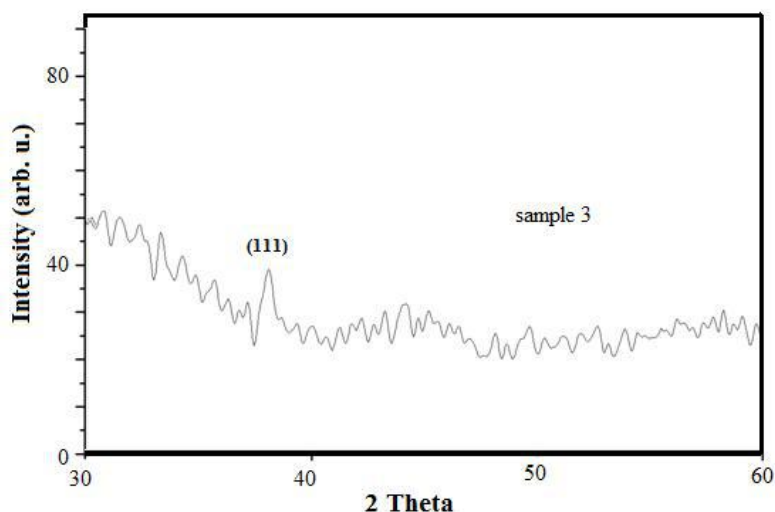


Figure 7. XRD analyze of sample 3.

The difference between oxygen stoichiometry can be resulted by changing in cell medium. Plasma arc in water medium prevents more oxidation in sample 2&3 compare to sample 1, that plasma arc was done in air medium. Additionally increase of the plasmon peak intensity in sample 2B compare to sample 2A shows monodispersity of nanoparticles in sample 1B that caused by adding  $H_2O_2$ .

#### 4. Conclusions

In this work silver NPs obtained by plasma arc method. The main goal of this paper was to observe the effect of changing the experimental medium, using  $H_2O_2$  and temperature on the crystalline structure and oxygen percent of silver NPs. Synthesis of nanoparticles at water medium in comparison with the air medium leads to less oxygen content in Ag nanoparticles. By adding  $H_2O_2$  to nanoparticle solution the average size of particles decrease and get monodispersed solution. After adding  $H_2O_2$  to solutions that were prepared in water medium, nanoparticles cannot have spherical shape like nanoparticles that prepared in air medium. Adding  $H_2O_2$  also increased the nanoparticle concentration with more crystallite.

The average crystalline size that resulted from XRD smaller in comparison with the average size that was measured by TEM, clear the resulted nanoparticle are not single crystallite. Besides XRD analysis demonstrates that in higher temperature the silver crystallites are bigger.

#### References

1. Khaydarov RA, Khaydarov RR, Gapurova O, *et al.* 2009; 11, 1193.
2. Sudeep PK, Kamat PV, *Chem. Mater.* 2005; 17, 5404.
3. H. Yin Hsu, NNIN REU Research Accomplishments, 2004; 68.
4. Prikhozhenko ES, Lengerta EV, Parakhonskiy BV, *et al.* ACTA PHYSICA POLONICA A. 2016; 129, 247.
5. Ashe B, Thesis MSc. National Institute of Technology Rourkela, India, (2011).
6. Henglein C. *Mater.* 1998; 10, 444.
7. Manshian BB, *Advanced Healthcare Materials* 2017; 6, 1601099.
8. Li HX, Lin MZ, Hou JG, *Journal of Crystal Growth*. 2012; 212, 222.
9. Hettiarachchi MA, Wickramarachchi PASR, *Sci J. Univ. Kelaniya*. 2011; 6, 65.
10. The Binh N, Thi Ly D, Thi Hue N, *et al.* VNU Journal of Science. 2008; Mathematics – Physics 24.
11. Wang B, Zhuang X, Deng W, *et al.* *Engineering* 2010; 2, 384.
12. Pol VG, Srivastava DN, Palchik O, *et al.* *Langmuir*. 2002; 18, 3352.
13. Hong-Liang F, Xiao-Yong G, Zeng-Yuan Z. *et al.* *Journal of the Korean Physical Society*. 2010; 56, 1176.
14. Amendola V, Osman M, Bakr F, Stellacci, *Plasmonics*. 2010; 5, 85.