# OBTAINING SILVER NANOPARTICLES BY SONOCHEMICAL METHODS

Vasile-Sorin MĂNOIU[1], Angel ALOMAN[2]

*Lucrarea de față se referă la obținerea unor nanoparticule de argint printr-o metodă sonochimică. Metoda presupune folosirea unei soluții de azotat de argint, AgNO₃, ce este supusă unui flux foarte intens de ultrasunete, ce conduce la apariția unor bule (cavități) microscopice. Acestea cavități se expansionează în timpul fazei de decomprimare a undelor ultrasonice și implodează violent în timpul fazei de compresie, generând presiuni si temperaturi deosebit de mari ce duc la formarea de nanoparticule. Experimentele de față au indicat că prin această metodă se pot obține nanoparticule de argint de formă sferică cu o bună uniformitate dimensională.*

*This work contains data about obtaining silver nanoparticles by a sonochemical method. This method involves using a solution of silver nitrate, AgNO₃, which is subject to very intense ultrasound flow leading to the emergence of microscopic bubbles (cavities). These cavities expand during the decompression phase of ultrasonic waves and implode with violence during the compression phase, generating extremely high pressures and temperatures, that lead to the formation of nanoparticles. Our experiments indicate that this method allows to obtain silver nanoparticles of spherical shape and size uniformity.*

**Keywords:** sonochemical synthesis, nanoparticles, silver

## 1. Introduction

Exploring ways of obtaining nanomaterials [1] and their properties [2] is crucial for future technical and technological development [3]. An important question is the synthesis of nanoparticles with different chemical composition, sizes, shapes and structures [4-8]. The applications of nanomaterials are so numerous, that practically all domains can benefit [9].

Obtaining the silver nanoparticles has attracted particular attention due to their unique size-dependent properties, such as optical, electrical, chemical, catalytic, and septic properties with potential applications in nanotechnology, medicine, catalysis, and biomaterials [10-15].

---

[1] PhD, National Institute of Research and Development for Biological Sciences INCDSB-Bucharest, spagiricus@yahoo.com
[2] Prof., Materials Science and Physical Metallurgy Department, University POLITEHNICA of Bucharest

Silver is known as one of the strongest antiseptic agents, antibacterial, anti microbial, antifungal, antiviral (if not the strongest) that have the unique quality to not generate mutations in pathogens that come into contact whith, because the patogens do not develop strains resistant to silver [3, 14].

Nanomaterials can be produced by different methods: mechanical, chemical, hydrothermal, sol-gel, chemical deposition in vacuum, pyrolysis, combustion, chemical coprecipitation, etc. By each of these methods particles defined by a certain dimensional morphology and distribution can be obtained. The characteristics of nanoparticles can be modified by the action of additional external factors, such as microwave heating, ultrasonic treatment, etc. [16-20]. Ultrasounds have a wide range of uses, like applications in development of nanoparticles using solutions of different chemical compounds. The production facility consists of a thermostatic chamber where the solution of salts or other compounds is introduced and a high power ultrasonic generator. The last one produces a powerful stream of ultrasonic energy that breaks the chemical bonds of compounds [20-27].

Generally, the generators use a 20kHz ultrasonic irradiation of $100W/cm^2$. The ultrasonic generator converts the 50Hz electric frequency in high energy and frequency energy flow. The electrical energy is transmitted to a piezoelectric transducer that converts it into mechanical energy.

The ultrasonic vibrations are intensified and focused through a ultrasonic probe in a very intense flow. The stream passes through the liquid causing alternatively a compression and a relaxation of the liquid. This change in pressure leads to the emergence of microscopic bubbles (cavities) that expand during the decompression phase and implode violently during the compression phase. Millions of shock waves are generated during the colapse, also high pressures and high temperatures being generated from the imploded cavities.

Although the cavitational colapse takes only a few microseconds and the amount of energy released by each cavity is minimal, the cumulative effect causes an excessively high level of energy that is released in the liquid.

According to the theory, the sonochemichal methods follow these steps [25]:

a) formation;

b) developing;

c) the implosive collapse of the microcavities obtained.

The acoustic waves crossing the liquids are generating a cavity phenomenon, accompanied by extreme effects: a local increase in temperature (5000K) and pressure (100MPa).

During the collapse of the bubbles, that takes place in less than a ns, temperatures of 5000-25000K are obtained, followed by a very rapid cooling, with a rate higher than $10^9$K/s. This rate is much higher than the conventional

method of rapid cooling ($10^5$-$10^6$ K/s) to obtain amorphous materials. This ultra-fast cooling process affects the formation and crystallization of the obtained substances. Therefore, in all cases using a volatil compound, where the reaction in gas phase is predominant, amorphous nanoparticles are obtained. The creation and production of amorphous rather than nanocrystalline nanoparticles can not be clearly explained, one explanation could be that fast kinetics does not allow nanocristals nucleation.

On the other hand, if non-volatile components are used, the reaction takes place with the formation of 200nm rings around collapsing bubbles. In this case, the sonochemichal reaction takes place in liquid phase, with amorphous and nanocrystalline nanoparticles formation .This depends on the temperature around the rings where the reaction takes place. The temperature inside these rings is smaller than inside the collapsing bubbles, but lower than the system temperature. It was estimated that the temperature around the rings is about 1900K.

The estimated size of the collapsing bubbles ranges from several dozens to several hundreds of microns.

Inside the bubbles a gaseous phase reaction occurs, and in the interface area surrounding the collapsing bubbles, a liquid phase reaction takes place. This region has a size of about 200nm and a collapsing temperature of 1900K. In these regions the reaction of non-volatile components such as salts occurs. In this case the reactions occur in liquid phase, producing amorphous or nanocristaline nanoparticles, depending on the temperature and the specific reactions.

The adiabatic implosion equation is [25]

$$T_{\max} = T_0\left[P_{ex}(\gamma-1)/P_b\right] \tag{1}$$

where
- $T_{max}$ – the temperature in the region of the collapsing bubble;
- $T_0$ – the temperature of the ultrasonicated liquid;
- $\gamma = C_p/C_v$;
- $P_{ex}$ – the external pressure and equals the sum of hydrostatic pressure and the acoustic pressure;
- $P_b$ – the gas pressure inside the cavity before collapsing.

The temperature affects the sonochemical reaction rate in two ways. On the one hand, lower temperatures cause a higher viscosity, which makes the formation of the bubble more difficult, and, on the other hand, the dominant effect is that at lower temperatures, higher rates will be achieved in sonochemical processes.

The average acoustic power of a sonic wave in the environment can be expressed by,

$$W = \frac{1}{2}\rho C V^2 S = \frac{1}{2}P_A V_0 S, \tag{2}$$

where:

- $W$ - average acoustic power of sonic waves traveling in the environment expressed in W;

  - $\rho$ - density $kg \cdot m^{-3}$;

- $C$ - speed of sonic waves, $m \cdot s^{-1}$;

- $V$ - vibration frequency of the particles, $m \cdot s^{-1}$;
- $S$ - area perpendicular to the traveling direction of sonic waves;
- $P_A$ - variation of the acoustic pressure, $Pa$;
- $V_0$ - volum, $m^3$.

The above equation shows that the increase of the variation of acoustic pressure $P_A$ increases the cavitaion phenomenon. Therefore, the particle diameter will decrease due to the increased cavitation effect.

A wide range of nanomaterials were obtained using the sonochemical method, such as metals, alloys, metal oxides, metal sulfides, metal nitrides, metal-polymer composites and so on.

## 2. Materials and methods

*Reagents* - Different concentrations of silver nitrate (*AgNO₃*) solution were used to obtain silver nanoparticles by a sonochemical method. A reagent *SigmaUltra* of purity> 99% and pure deionized water solution was used.

*Apparatus* - Ultrasonic waves were generated with an ultrasonic processor type *Sonics Vibra cell VCX 750* fitted with a 3 mm titanium probe.

A *TEM Philips EM 208S* microscope equipped with a *Veleta* TEM camera, and *iTEM Olympus Soft Image System* software for imaging acquisition was used for the investigation of the nanoparticles.

*The working method* - The working temperature chosen was 30°C and it was measured with the temperature probe of the ultrasonic generator. To maintain their temperature, the salt solutions were ultrasonated in a double-wall glass container cooled with water; the ultrasonic generator's software allowed setting and maintaining a preset temperature. The generator frequency was *20kHz* and the signal amplitude was 20% of *182 μm*, respectively *36,4 μm*.

### 3. Results

Experiments of obtaining silver nanoparticles have been carried out in the conditions specified in Table 1.

*Table 1*

**Experiment parameters for obtaining the silver nanoparticles using ultrasound**

| No. | AgNO$_3$ molarity [$M$] | Volume of Solution [$ml$] | Temperature [$°C$] | Duration [$h$] | Amplitude of Ultrasonic waves [$\mu m$] | Average power [$W$] | Total energy used [$J$] |
|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 1,5 | 30 | 1 | 114 | 2,5 | 9934 |
| 2 | 0.01 | 1,5 | 30 | 1 | 114 | 2,5 | 8122 |
| 3 | 0.001 | 1,5 | 30 | 1 | 114 | 2,5 | 7680 |

A working time of 1h was chosen. *TEM* microscopy techniques were used to investigate the samples.

For the transmission electron microscopy examination, grids of 200 mesh copper mesh were used, having a film of formvar applied upon.
The solution was ultrasonated and used to cover the grids. After 15 minutes the grids were washed by driping distilled water and were dried on filter paper.
The results of the TEM microscopy investigation of the obtained silver nanoparticles are presented in the micrographs in Fig.1, 3, 4.
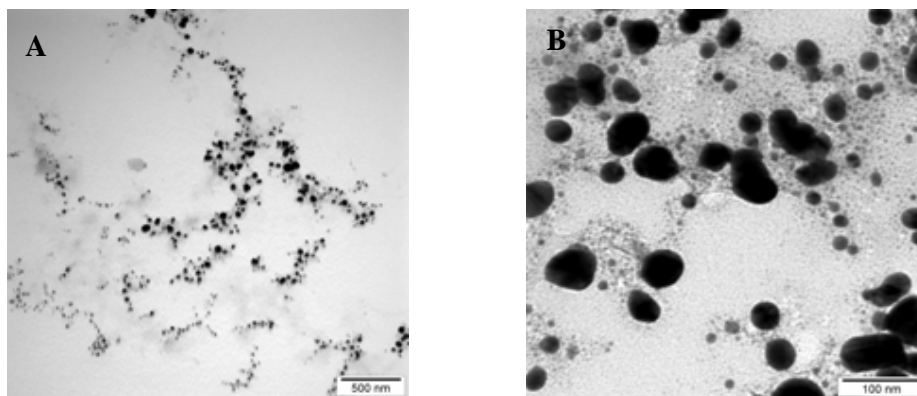


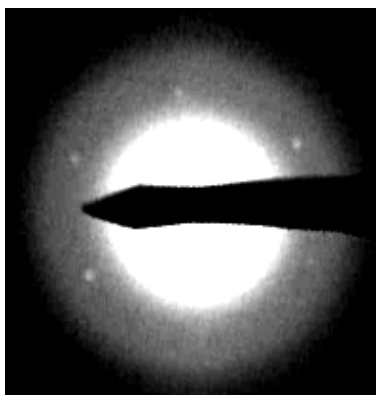Fig.1. Particles obtained by ultrasonication of *AgNO$_3$ 0.1M* solution (A, B)

Fig.2. Electron diffraction of particles obtained by ultrasonication of *AgNO₃ 0.1M* solution. The spots indicate the cristalinity of particles
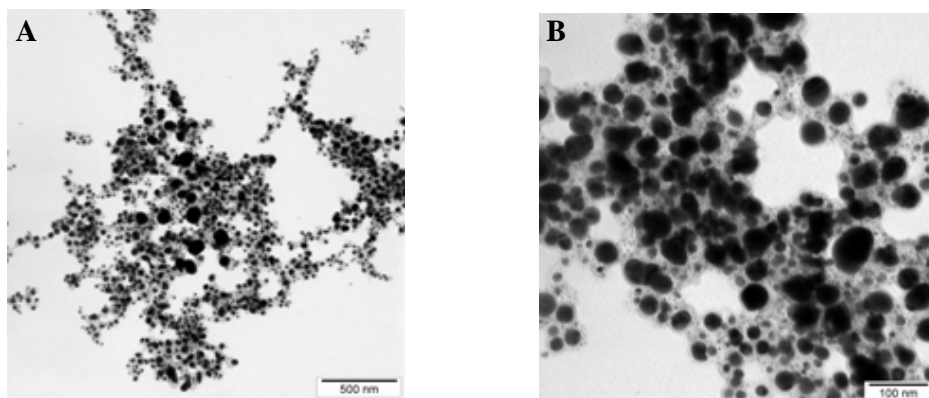


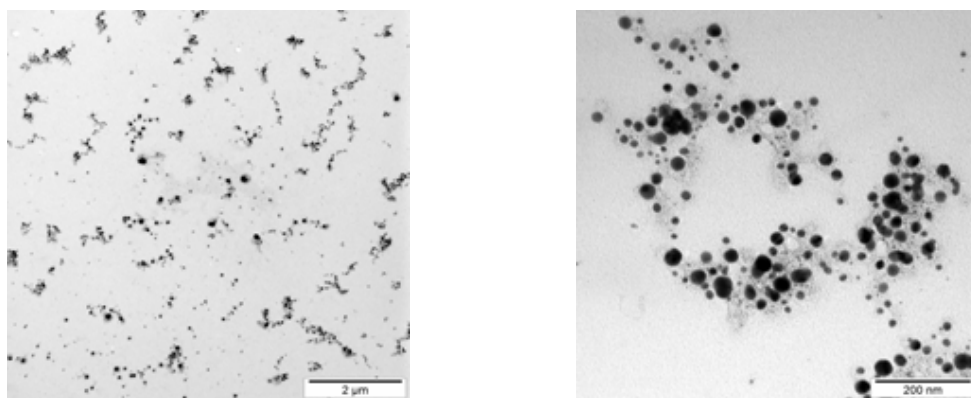Fig.3. Particles obtained by ultrasonication of *AgNO₃ 0.01M* solution (A, B)



Fig.4. Particles obtained by ultrasonication of *AgNO₃ 0.001M* solution (A, B)

## 4. Discussion and Conclusions

The transmission electron microscopy images have emphasized that the nanoparticles obtained had mainly a spherical or ellipsoidal shape (Fig. 1, 3, 4).

From electron diffraction image performed on the nanoparticles the spots observed are indicating the cristalinity of the nanoparticles (fig.2).

*Table 2*

**Values of measurements on nanoparticles produced by ultrasonic method of silver nitrate solutions**

|  | Dilution $AgNO_3$ 0.1M | | Dilution $AgNO_3$ 0.01M | | Dilution $AgNO_3$ 0.001M | |
|---|---|---|---|---|---|---|
|  | No. of measurements 274 | | No. of measurements 345 | | No. of measurements 214 | |
|  | Area [nm$^2$] | Max. Diameter [nm] | Area [nm$^2$] | Max. Diameter [nm] | Area [nm$^2$] | Maximum Diameter [nm] |
| Min. Value | 4.15 | 2.3 | 4.52 | 2.4 | 3.46 | 2.1 |
| Medium Value | 211.04 | 8.09 | 135.50 | 6.26 | 151.33 | 8.08 |
| Max.Value | 5712.35 | 76.11 | 9439.58 | 108.46 | 2896.163 | 52.39 |
| Standard Deviation | 734.50 | 13.37 | 650.09 | 11.03 | 377.804 | 10.45 |

The analysis of TEM microscopy images shows that there are no significant differences in the form of structures obtained by ultrasonication of solutions of different concentrations of silver nitrate.

From Table 2 it may be noted that the average size of nanoparticles obtained is around 7 nm, at least about 2 nm and 100 nm maximum.

Our results show that the sonochemical method for silver nitrate allows the formation of nanoparticles with a nonuniform dimensional distribution and a spheroidal shape.

R E F E R E N C E S

[1] *A.P. Alivisatos,* Perspectives on the physical chemistry of semiconductor nanocrystals. J. Phys. Chem. 1996, 100, 13226-13239
[2] *J.R. Morones, J.L. Elechiguerra, A. Camacho, K. Holt, J.B. Kouri, J.T. Ramirez, M.J. Yacaman,* Nanotechnology 2005, 16, 2346-2353
[3] *A. Elaissari* (Ed) Colloidal biomolecules, biomaterials, and biomedical applications.New York, Marcel Ekker, INC., 2005, 488p

[4]  *C. Burda, X. Chen, R. Narayanan, Ma El-Sayed*, Chemistry and Properties of Nanocrystals of Different Shapes. Chemical Reviews (Washington, DC, United States) 2005, 105:1025-1102.

[5]  *C.N.R. Rao, A.K. Cheetham*, Science and technology of nanomaterials: Current status and future prospects. J. Mater. Chem. 11, 2887 (2001)

[6]  *A. Aloman,* Bazele ştiinţei materialelor (Fundamentals of materials science) Bucureşti, Printech, 2003, 1595p

[7]  *O. Popa, M. Drugulescu, V.S. Mănoiu, N. Babeanu, N. Zambila,* Bionanoparticule metalice. Obţinere şi aplicaţii. (Metallic bionanoparticles. Obtaining and applications). Bucureşti, Editura DO-MINO, 2008, 57 p

[8]  *K.S. Kumar, H. Van Swygenhoven B, S. Suresh*, Mechanical behavior of nanocrystalline metals and alloys, Acta Materialia 51 (2003) 5743–5774

[9]  *E.J. Fernandez, J. Garcıa-Barrasa, A. Laguna, J.M Lopez-de-Luzuriaga, M. Monge, C. Torres*, The preparation of highly active antimicrobial silver nanoparticles by an organometallic approach, Nanotechnology 19 (2008) 185602 (6pp)

[10] *W. H.C.,* Observation of Growth of Human Fibroblasts on Silver Nanoparticles, Journal of Physics: Conference Series, 61, p. 445–449, 2007

[11] *E.J. Fernandez,* The preparation of highly active antimicrobial silver nanoparticles by an organometallic approach, Nanotechnology, 19, 2008

[12] *J.L. Elechiguerra,* Interaction of silver nanoparticles with HIV-1, Journal of Nanobiotechnology, **vol. 3**, 2005

[13] *P. Gopinath,* Implications of silver nanoparticle induced cell apoptosis for in vitro gene therapy, Nanotechnology, 19, 2008

[14] *J.R. Morones,* The bactericidal effect of silver nanoparticles, Nanotechnology, 16, 2005

[15] *A. Schrand,* Can silver nanoparticles be useful as potential biological labels?, Nanotechnology, 19, 2008

[16] *Tang S.,* Ultrasonic electrodeposition of silver nanoparticles on dielectric silica spheres, Nanotechnology, 18, 2007

[17] *S. Avivi,* The preparation of magnetic proteinaceous microspheres using the sonochemical method. Biochimica et Biophysica Acta, 1527, p.123-129, 2001

[18] *A.R. Caruso,* Sonochemical formation of colloidal platinum. Colloids and Surfaces, 169, p.219-225, 2000

[19] *A. Gendaken,* Using ultrasound radiation for the preparation of amorphous nanophase metals, alloys and oxides

[20] *C, Jingquan,* Preparation and characterization of silver colloids with different morphologies under ultrasonic field, Front. Chem. China., 4, p.418−422, 2006

[21] *F. Dang,* Sonochemical synthesis of monodispersed magnetite nanoparticles by using an ethanol–water mixed solvent, Ultrasonics Sonochemistry, 16, p. 649–654, 2009

[22] *P.B. Filson,* Sono-chemical preparation of cellulose nanocrystals from lignocellulose derived materials, Bioresource Technology, 100, p.2259–2264, 2009

[23] *Koltyoin Y.,* Sonochemical preparation of amorphous nickel. Journal of Non-Crystalline Solids, 201, p.159-162, 1996

[24] *T. Fujimoto,* Sonolytical preparation of various types of metal nanoparticles in aqueous solution. Scripta Materialia, 44, p.2183-2186, 2001

[25] *A. Gendaken*, Sonochemistry and its application to nanochemistry. Current Science, **vol. 85**, nr. 12, p.1720-1722, 2003

[26] *Z. Jia*, Room temperature fabrication of single crystal nanotubes of CaSn(OH)$_6$ through sonochemical precipitation, Journal of Colloid and Interface Science, 334, p.202–207, 2009

[27] *R.V. Kumar,* Sonochemical synthesis and characterization of Ag$_2$S/PVA and CuS/PVA nanocomposite, Ultrasonics Sonochemistry, 9, p.65-70, 2002.