Does appearance matter? Impact of particle shape on nanosilver characteristics

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1. Introduction
Nanotechnology is a rapidly developing field of science, and real interest in nanotechnology began to grow in the early 1990s. The nano prefix, originating from the Greek language, refers to the order of magnitude that nanotechnology deals with. The invention of the scanning tunnel microscope (STM) was a real breakthrough that led to rapid expansion of this field, and enabled conducting research at atomic level [1]. The basic task of nanotechnology is the development, fabrication and implementation of materials, the common feature of which is their dimension, sized between 1 to 100 nanometres. The advantage of nanocompounds are their properties, which differ from the characteristic properties of individual atoms or crystals. This is due to the dimensions of the particle, the diameter of which is within the range corresponding to individual atoms ($10^{-9}$ m) and crystals ($10^{-7}$ m), the features being therefore different from those characteristic of boundary structures [2].

The properties of nanocrystalline materials are determined by physical parameters, such as: size, shape, composition and structure. In fact it is possible to acquire the desired properties of nanostructures by controlling one of the parameters mentioned, with which individual features of the material are closely bound. Investigations carried out using localized surface plasmon resonance (LSPR) and surface-enhanced Raman spectroscopy (SERS) have shown that the shape and structure of silver and gold particles play a key role in the determination of the main features of a material, such as, for instance, chemical activity [3].

The particles of nanomaterials may take on different shapes, including spheres, tubes, bars and prisms. One of the tasks of nanotechnology is to combine these structures into larger entities and systems, while controlling at the same time the quality of the developed nanomaterials [4]. Nanotechnology brings about many benefits. The outstanding properties of nanocompounds have contributed to the intensification of their manufacture, as the range of nanocompound applications in various fields of life has broadened vastly. Nanoparticles are today used in electronics, biomedicine, pharmacy, cosmetics, catalysis and other applications due to the ease of conducting their manufacture, ability to model their properties, high reactivity and large surface area [5].

One of the most widely applied nanomaterials is nanosilver (NAg), the use of which is increasingly commercially profitable [6]. Man started using silver even before the Neolithic Revolution. Ancient Greeks used silver vessels for storing water and other liquids. The 8th century saw novel methods of silver application in the healing art. Before the rise of nanotechnology advantage was taken of only the basic form of silver; after silver was obtained in the nano form, its properties positioned it among the most profitable nanomaterials. From the scientific point of view nanosilver has a number of advantages, such as: chemical stability, thermal conductivity, catalytic and antibacterial activity [7]. Nanosilver properties strongly depend on the size and shape of its particles; a great stress is therefore laid on research focused on the synthesis and characterization of silver nanoparticles of various geometry [8].

2. Preparation of nanocompounds
Research on preparation and characterization of nanocompounds based on noble metals, such as gold or silver, has been conducted in many research centres since the very beginnings of nanotechnology [9]. Metal nanoparticles play a distinct role in various fields of life, including photography, catalysis, biological assay, optoelectronics, medicine. Nanomaterials also found use in surface-enhanced Raman spectroscopy (SERS). Nanocompounds can also be used in the preparation of magnetic fluids. Properties of nanoparticles are determined primarily by the size, shape, composition and structure of the compound [10].

Intense attempts to develop methods of nanoparticle synthesis, while observing their size, shape, composition and surface structure, have resulted in very useful properties of nanocompounds. For instance, controlling the shape of a nanoparticle is one of the major factors that determine nanoparticle properties. A nanosilver particle with a cubic structure shows the highest activity in catalysing styrene oxidation [11]. Other forms of noble metals occurring in the nano scale include: prisms, discs, plates, triangles, bars and nanotubes [9]. In view of the dependency of the properties on the structure of particles, new methods of particle shape-controlled methods of nanocompound synthesis are sought [11].

2.1. Nanosilver preparation methods
Nanotechnology and modern synthetic chemistry are the main sources of nanoparticular silver. Many methods of nanosilver preparation are known (described in detail). Each of them has its characteristic yield and limitations. The selection of the method of obtaining nanosilver has an impact on the final characteristics of the particle, such as: diameter, size, shape, stability, presence of ligands and agents protecting the core. In addition, depending on the applied method of nanoparticle silver synthesis, the yield of the chemical reaction and amount of generated contamination vary. Despite the considerable number of known methods of nanosilver synthesis, only a few are applied in practice. The most preferred method of nanosilver production is by reducing silver nitrate with a suitable reducing agent, e.g. sodium borohydride. Another equally widespread method is photoreduction by UV irradiation. Mentions of the so-called green methods of obtaining nanosilver can also be found in the literature. However, research laboratories are still working on developing truly environmental-friendly methods of synthesis [12].

The most important current issue in nanotechnology is to find such a method of obtaining nanosilver that would enable generation of a large number of particles of controlled size and shape [13].

One of the most widespread methods of obtaining nanosilver is chemical reduction reaction. The procedure is based on the reduction of silver nitrate or other salt of silver, using a reducing agent, usually sodium borohydride (NaBH₄) or hydrazine (N₂H₄). The process is conducted in the presence of a stabilising agent, such as sodium dodecylsulphonate, in order to prevent the formed nanosilver particles from associating into larger agglomerates. The main advantage of this method is the low tendency of nanoparticles to aggregate, and additional benefits are the ease of conducting the process and relatively inexpensive reagents and equipment [14, 15]. The decisive effect on the properties of the products is produced by: initial concentration of the silver salt, ratio of molar concentrations of reducing agent and silver salt, and concentration of the stabilising substance [15, 16].
Another method of preparing nanoparticulate silver is photochemical reduction, which allows mixing of all substrates before the initiation of the reaction. This method comprises an immediate reduction of silver cations, while the nanoparticles formed are trapped kinetically [17]. Kempa et al. presented a method of nanosilver preparation, consisting in the reduction of silver perchlorate (AgClO$_4$) in the presence of N-methylfinedipine and under UV irradiation. The researchers obtained silver nanoparticles of the size range of $1 \div 7$ nm [18].

Another important method of obtaining nanosilver is laser ablation, which includes a liquid-solid interface reaction [19]. In this process a pulsed laser beam is directed onto the surface of the solid, initiating thereby the “expelling” of the material from the solid surface. The expelled material is conveyed to the surrounding solution of the reducer: this is the mother liquor; it can be ethylene glycol or diethylene glycol. Final properties of the product depend on the parameters of the laser, as well as the concentration of the mother liquor. The major advantage of this method is the purity, stability and spherical shape of the nanoparticles obtained [17, 20].

Reetz and Helbig were the first to propose an electrochemical method of obtaining nanosilver. It comprises the following steps: anodic metal dissolution, reduction of the generated intermediate salt of metal on the cathode, and stabilisation of the particles formed with trialkylammonium salts. The strength of this method is the exceptional purity of the generated nanoparticles and the ability to control the shape and size of particles by continuous equalising of density without the need to add surfactants. What’s more, this method may be effected by means of simple and affordable equipment [21].

An interesting solution are the so-called green (that is environment-friendly) methods of obtaining nanosilver, the essence of which is, for instance, the application of Bacillus subtilis bacteria that provide an enzyme, nitrate reductase. The knowledge about the mechanisms of environment-friendly methods of obtaining nanosilver is incomplete. However, scientists suppose that reduction of Ag$^+$ ions is caused by the enzyme, peptides and proteins [22]. The basic advantage of the method is the ease of its implementation, as well as the ability to conduct the process on a large scale [23].

3. Types of nanoparticles

The recent decade has seen successful synthesis of nanometals of various shapes. The major shapes include: spheres, cubes, bars, tubes, tetrahedrons, octahedrons, decahedrons, icosahedrons, prisms, pyramids, stars, cages and other. General classification of nanomaterials reflects their composition. There is a distinction between mono- and bimetallic structures, metal oxides, semiconductors, hybrid structures, composites and other [24]. Glotzer and Solomin made an attempt to define a number of rules for categorising particles in order to unify the abundance of the various shapes and types thereof [25]. Further in this paper we present one common method of nanomaterial classification based on the directions of particle growth; three groups of structures, which depend on the number of dimensions: a) one-dimensional (1D) – growth restricted to one dimension – this group includes, for example, nanobars and nanotubes; b) two-dimensional particles (2D) – growth proceeds in one plane, but in two dimensions – this category includes planar triangles, planar hexagons, discs, ribbons, strips; c) three-dimensional particles (3D) – particle grows in three directions simultaneously – this set includes tetrahedrons, cubes, octahedrons, decahedrons, icosahedrons, prisms, nanocages, as well as irregular structures, i.e. bumpy, thorny, bristly particles [24]. Examples of 1D, 2D and 3D nanoparticles are shown in Table I.

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Shape</th>
<th>Diagram</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>tube with rectangular or octagonal cross section</td>
<td>![Diagram](410x629 to 505x657)</td>
<td>Pb, In, Sn, Sb, Fe, Co</td>
</tr>
<tr>
<td></td>
<td>tube with pentagonal cross section</td>
<td>![Diagram](414x660 to 500x711)</td>
<td>Pd, Ag, Au, Cu</td>
</tr>
<tr>
<td></td>
<td>disc</td>
<td>![Diagram](423x555 to 460x583)</td>
<td>Sn, Co</td>
</tr>
<tr>
<td>2D</td>
<td>planar triangle or hexagon</td>
<td>![Diagram](436x420 to 474x447)</td>
<td>Pd, Ag, Au, Cu, Pb, Bi, Co, Ni</td>
</tr>
<tr>
<td></td>
<td>ribbon</td>
<td>![Diagram](437x349 to 478x383)</td>
<td>Ag, Au</td>
</tr>
<tr>
<td></td>
<td>tetrahedron</td>
<td>![Diagram](442x314 to 473x346)</td>
<td>Ag, Au, Pt, Rh</td>
</tr>
<tr>
<td></td>
<td>cube</td>
<td>![Diagram](442x455 to 473x479)</td>
<td>Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe</td>
</tr>
<tr>
<td></td>
<td>octahedron</td>
<td>![Diagram](444x266 to 476x310)</td>
<td>Pd, Ag, Au</td>
</tr>
<tr>
<td></td>
<td>decahedron</td>
<td>![Diagram](445x594 to 474x624)</td>
<td>Ag</td>
</tr>
<tr>
<td></td>
<td>icosahedron</td>
<td><img src="513x477" alt="Diagram" /></td>
<td>Pd, Au</td>
</tr>
<tr>
<td>3D</td>
<td>sphere</td>
<td><img src="518x439" alt="Diagram" /></td>
<td>Ag</td>
</tr>
<tr>
<td></td>
<td>prism</td>
<td><img src="520x497" alt="Diagram" /></td>
<td>Pd, Ag, Pt</td>
</tr>
</tbody>
</table>

4. Nanosilver properties vs. particle shape

Although it is now possible to control the size and shape of nanosilver particles, the yield of processes is still a great challenge. Nanoparticulate silver is obtained in small concentrations only. However, particles of desired shape can be obtained, and consequently the properties of the product can be controlled. In nanostructures, where hundreds or thousands of atoms or molecules form a whole, shape of the particle is seen as the key factor determining the properties of the nanomaterial [8]. Individual shapes of silver nanoparticles depend on reaction conditions, including temperature, concentration of substrates and molar ratio thereof [26]. The final appearance of the particle also depends on the relations between the valency, stoichiometry and geometry of the substrates, as well as on the way the individual silver atoms are arranged. Of large significance is also the reactivity of molecules and the value of surface energy, which has a considerable impact on the shape of the nanoparticle; the same cannot be said of the energy of the bonds [24].
Nanotubes

The scientists’ attention is now drawn by the metals in the form of nanotubes, due to their enormous potential as electrical conductors. A carbon conductor is known, the shape of which is in the form of a nanotube. Another reason is the search for minute conducting elements that could be applied in nanoelectronics. Nanotubes are nowadays produced from various metallic and semiconductor materials using various methods, of which the chemical method provides products of a perfect crystalline structure. Graff et al. obtained silver nanotubes using a novel method of chemical reduction of silver ions in an aqueous solution of an electrolyte [27].

Nanotube particles have a relatively large length to thickness ratio, in some cases reaching 2500, whereas the thickness of particles varies between 13 and 150 nm. The thickness of a particle usually remains constant along its entire length, except for a few cases, where thickness gradually changes. The tips of particles are rounded. Graff et al. have established that silver nanotubes stored in a cool and dark place remain stable for several days. They also found that this form of nanosilver becomes unstable upon reaction with sulphur compounds contained in air: nanotubes then spontaneously break up into smaller pieces [27].

Tests have demonstrated that nanosilver in the form of decahedrons has the ability to elongate and take on a structure that resembles a tube. This happens when reaction conditions are favourable for the stabilisation of the newly formed structure. The presence of surfactant molecules is essential. These molecules attach strongly to the surface of silver and initiate the process. Selective deposition of silver atoms causes uniaxial elongation of decahedron particles into a twin-like nanotube structure. The new shape is stabilised owing to chemical reactions of the surfactant, the role of which may be assumed by e.g. sodium dodecyl sulphonate [11].

Another method of obtaining nanotubes was developed by Murphy et al. It consists in adding silver nanoparticles, ca. 4 nm in size, to a solution containing silver precursors, reducing agents and surfactant molecules, e.g. cetyltrimethylammonium bromide. This method turned out to be particularly effective as regards the control of nanosilver particle shape during the synthesis process [28].

Hirai et al. [29] have come to a conclusion that in silver nanotubes with axes shorter than 1 µm, the space between metal atoms is small, and it is then difficult to form an electrical conductor out of them, and therefore such structures show high resistance to conduction. However, when the length of the main axis of a particle is larger than 500 nm, then the nanotubes can easily be joined together, which has a disadvantageous effect on electrical stability. Solutions of silver nanotubes developed by researchers can be used as a water ink for ink printers or printers for ATMs. They can also be used in antistatic agents for display screens, electrodes for flexible screens, electrodes for solar cells and in antistatic coatings [29].

In order to study the optical properties of silver nanotubes, researchers carried out investigations using localized surface plasmon resonance (LSPR), which proved that silver particles show strong plasma absorption and Rayleigh scattering of visible light. What’s more, it was found that electron oscillations were limited by the size and shape of the nanosilver particle. In contrast to spherical nanosilver particles, which are characterized by a single plasma absorption band, one-dimensional nanotubes have two main absorption bands. The band of higher energy corresponds to absorption and scattering along the shorter axis of the particle, whereas the band of lower energy is related to absorption and scattering along the longer axis of the nanotube. In addition, electromagnetic field is stronger near the tips of the nanoparticle, making it an interesting substrate for surface-enhanced Raman spectroscopy (SERS). A common desire to implement nanomaterials in microdevices, or even nanodevices, calls for a reflection on their electronic properties. In their research, Heath et al. obtained a high-density electrode consisting of platinum nanotubes. Eventually the device had a density of 60 tubes per 100 µm, it had a regular structure and was used as a high-frequency resonator.

In order to introduce nanotubes in the microelectronics industry it is necessary to study the mechanical properties of nanomaterials. Strength, hardness and modulus of elasticity of nanotubes can be measured experimentally by means of a variable atomic force microscope. Boland et al. measured the mean strength of silver nanotubes ca. 40 nm in diameter and found that it was 0.88 GPa, i.e. twice higher than the strength of solid silver [28].

Planar nanotriangles

Interest in the synthesis of planar triangular nanoparticles of silver grew since the pioneering work of Jin et al. of 2001, who carried out a photoinduced conversion of nanospherical silver particles into nanoprisms during several hours [30].

Many studies have been conducted on the synthesis and characterization of two-dimensional silver nanoparticles, i.e. planar triangles and planar hexagons. Mirkin et al. presented a method of obtaining a solution of planar silver nanoparticles by reducing silver nitrate AgNO₃ with sodium borohydride, NaBH₄, in the presence of citrate and bis[p-sulphonatophenyl]phenylphosphine dihydrate dipotassium salt (BPSP). The substrates were subjected to controlled action of a laser. The induced photochemical reaction resulted in the transformation of the spherical silver particle into a planar triangular one. The size of the nanotriangles can be controlled by using light of various wavelengths.

Other method was applied by Yin et al., who synthesized silver nanotriangles by conducting a reaction of reducing aqueous solution of silver nitrate, AgNO₃, with sodium borohydride, NaBH₄, in the presence of trisodium citrate, polyvinylpyrrolidone (PVP) and H₂O₂. Exposing all substrates to 365 nm UV light caused change in the colour of the solution – from blue, through pink, to yellow, which reflected morphological changes: vertices of the triangular particles were initially truncated, and the particle finally took on the shape of a nanodisc. By increasing the molar ratio of AgNO₃ to PVP, initial concentration of AgNO₃, temperature of the process and reaction time, it is possible to obtain hexagonal planar nanoparticles of silver at a yield of ca. 95%. In order to evaluate the effectiveness of other surfactants, the researchers replaced PVP with polyethylene glycol (PEG) and sodium dodecyl sulphonate (SDS). This, however, resulted in the particles taking on irregular shapes, while planar nanoparticles could not be formed on every attempt. PVP is therefore a key agent in reactions leading to two-dimensional nanoparticles of silver [11, 31].

Nanoribbons

Nanoribbons represent another group of nanostructures, which resemble flat creased ribbons of constant thickness along their entire length. Due to asymmetrical geometry, synthesis thereof is very demanding, and only a few attempts to obtain nanoribbons proved successful [11]. Qi et al. developed a highly efficient method of pure silver nanoribbon synthesis [32]. They reduced silver nitrate (AgNO₃) at 4°C with ascorbic acid in an aqueous solution of polyacrylic acid (PAA). Images of the product obtained with a transmission electron microscope (TEM) confirmed the ribbon structure of nanosilver, and indicated its high purity reaching 100%. Examination by electron scanning microscope has confirmed that all silver nanoparticles were of similar geometry. The width of particles was within 60 and 100 nm, and thickness was from 30 to 40 nm [32].

He et al. obtained silver nanoribbons of similar dimensions, but on a larger scale. They carried out chemical reduction of silver nitrate (AgNO₃) with N,N-dimethyldiformamide (DMF) in the presence of polyvinylpyrrolidone (PVP). The key factors that had an effect on the results included: initial concentration of silver nitrate,
AgNO₃/PVP molar ratio, process temperature and time. Researchers have established that the reaction between these substrates under optimum conditions favours the formation of silver nanoribbons. What’s more, their final shape can be controlled by varying the AgNO₃/PVP ratio. The length of these particles can be increased to several micrometres, in some cases to as much as several dozen micrometres! Photographs of the synthesized silver nanoparticles, taken under higher magnification, suggest that two nanoribbons can be intertwined, which indicates the occurrence of strong interactions between PVP and silver atoms. Microphotographs also indicate the uniformity of the width of nanoribbons and the lack of colour contrasts along the transverse section of the particle. In addition, results of analysis indicate that longer particles are susceptible to breaking into two separate smaller silver nanoribbons. The destroying force may have been the fractionating centrifugation used by the researchers to separate the mixture into fractions. It is also known that particles can combine into a larger, more stable structure. The results of experimental tests show that silver nanoribbons are more stable than other two-dimensional particles. Structures like this can in future be used in the manufacture and finishing of devices fabricated in the nanoscale [31].

Another group of researchers, Xia et al., has transformed in thermal processes the spherical shape of nanosilver into ribbon shape. The product, however, contained other nanostructures that could not be readily removed.

It was found that nanoribbons exhibit similar properties to those of silver nanotubes. Zhao et al. suggest that overlapping nanoribbons form a structure applicable in the construction of nanodevices [33].

Scientists say that electron deposition is an facile and economic method of producing silver nanoribbons on a large scale, and the results of which can be controlled by varying the voltage applied. In view of the high electrical conductivity of nanosilver, researchers promote its applications in microelectronics and optical and magnetic devices [33].

**Nanodiscs**

Chen et al. developed a method of silver nanodisc generation in a chemical reaction involving a phase transition [34]. It was found that nanodiscs had very strong surface plasmon bands at ca. 475 nm. What’s more, in the process of mild ageing these bands can be tuned within 420 ± 560 nm, and the upper surface of the nanoparticle can be covered with a monolayer of long-chain organic molecules, which in some cases is very desirable. Due to the nanoscale of dimensions of silver nanodiscs, these particles, as was the case of other shapes, can be used as a building material in modern nanoelectronics.

Synthesis includes two main steps. The first step, consisting in the formation of truncated silver nanotriangles, arises indirectly through the growth of nanosilver grains in the presence of N-cetyl-N,N,N-trimethylammonium bromide (CTAB). The second step is the ageing for 4 hours of the solution of triangular silver nanoparticles at 40°C. The measured distribution of particle size also indicates that the mean diameter of a particle is 59 ± 10 nm. Measurements using transmission electron microscopy indicated that the thickness of particles was 20 nm, whereas its diameter varied between 50 and 90 nm. In order to verify that these particles had a flat structure, a test was performed consisting in projecting (presenting graphically) the particle onto a plane, which showed that the shape of the projection of the particle becomes ellipsoidal when the angle of incidence changes from +60° to -60°. This indicates that silver nanoparticles are planar rather than spherical. Another proof of the flat structure of nanodiscs is their self-assembly into a chain structure, which facilitates the estimation of their thickness (ca. 26 nm). Measurement of voids between adjacent particles has revealed that the mean distance between these particles ranges from 3 to 3.6 nm. The mean length of the C₁₄ chain (derived from CTAB) is ca. 1.8 ± 1.9 nm, and thus the distance between adjacent nanodiscs is two times larger. This indicates that every silver nanoparticle can be covered with a monolayer of CTAB particles, with the CH₃-N⁺ group linked to the silver surface and the alkyl chain projecting outward into the solution. Strong interactions between alkyl chain and nanodiscs induce the grouping of particles. Analysis of nanodisc structure indicates that the surface of such particles can have the lowest surface tension in comparison to other nanosilver particle shapes. In addition, the monolayer surface adsorption of CTAB plays an important role in decreasing that tension and stabilization of particles. Chen et al. state that the ageing process in the synthesis procedure has a significant effect on the shape of nanosilver particles. In order to verify the above, tests were performed on a few samples obtained after differing ageing times at 40°C. Images of the product obtained with a transmission electron microscope show that the outline of particles in the sample that was not subjected to ageing is triangular in shape. It is interesting that these particles are surrounded by smaller ones, less than 10 nm in size. Researchers say that these small particles play a significant role in the growth of the larger, triangular particles. With increasing ageing time, from 5 min. to 4 hours, the shape of the particle changes from that of a truncated planar triangle to a circle (disc), and also the thickness of the nanoparticle changes: 24 ± 8 nm after 5 min. and 226 ± 3.4 nm after 4 hours. In addition, it was established that after prolonged ageing, much longer than 4 hours, silver nanoparticles take on a spherical shape. What's more, when the research team increased the ageing temperature to 80°C, the particles dissolved, which was visually manifested by the fading of the colour of the solution. Changes in the shape of silver nanoparticles are also disclosed during absorption spectrophotometry measurements. Before the sample is aged, the spectrum of truncated triangles exhibits three main peaks: 584, 444 and 351 nm. As the ageing time changes from 5 min. to 4 hours, the 584 nm peak shifts towards violet, indicating change of particle shape from triangular to circular. After 57 hours of ageing the spectrum has only one peak, at 420 nm, which corresponds to a spherical particle.

It may be noted that nanodiscs are similar in size, which is not certain in the case of e.g. nanotubes. This property is extremely valuable if nanodiscs are to be applied in the construction of nanodevices [34].

**Nanocubes**

Synthesis of high quality nanocubes is extremely difficult. However, in 2002 Sun and Xia published a paper describing successful preparation of silver nanocubes in the polyol process [35]. The essence of this synthesis is the chemical reduction of silver nitrate (AgNO₃) with ethylene glycol at elevated temperature. Images from a scanning electron microscope (SEM) and transmission electron microscope (TEM), enabled the measurement of the length of the edge of nanoparticles, which was ca. 175 nm. Microphotographs disclose that each particle of nanosilver has a perfect cubic structure with smooth surfaces and slightly truncated vertices. What’s more, tests have proven that each nanocube had a crystalline structure and was coplanar with adjacent nanocubes. By varying the time of the reaction and concentration of substrates it is possible to adjust the final size of nanoparticles, which in the Sun and Xia’s experiments varied between 50 and 200 nm. The polyvinylpyrrolidone (PVP) used in the process assumes the role of the surfactant which prevents the nanocubes from aggregation [10, 35].

Another solution was discovered by Kundu et al., who synthesized silver nanocubes on a large scale by reducing AgNO₃ with microwave radiation in a of polystyrene sulphonate (PSS) solution in the presence of gold seed particles [36].

These examples prove that to carry out a successful synthesis of silver nanocubes it is necessary to select the proper surfactant that
has a direct effect on the growth of particles in different directions. In addition, if additional substances that can be adsorbed on the surface of nanosilver take part in the reaction, then an extended nanocubic structure may be formed, leading eventually to elongated irregular shapes [11].

**Nanospheres**

The most widespread methods of obtaining silver nanoparticles of spherical shape include chemical reduction of silver nitrate (AgNO₃) with ascorbic acid, sodium borohydride or citrate as the reducing agent. However, in the case of citrates, the product is a mixture of silver nanospheres and nanotubes. If sodium borohydride is used in the reaction, then the geometry of the final silver nanoparticles is dominated by relatively small nanospheres, the diameters of which are below 10 nm. The disadvantage of the above scheme is the fact that the growth of the desired particles cannot be readily controlled by changes in the initial concentration of substrates, pH or temperature of the process. However, Qin et al. have proved in their research that the size of silver nanospheres can be changed when ascorbic acid is used as the reducing agent. The size of nanoparticles was adjusted by increasing the value of pH from 6.0 to 10.5. The diameters varied in this case within the range of 73–31 nm. Changes of pH were adjusted with citric acid and solution of NaOH. UV-Vis spectroscopic investigations have indicated that silver nanospheres obtained at pH values of 6.0, 7.0, 8.0, 9.0, 10.0 and 10.5 were related to the following absorption peaks: 480, 453, 442, 433, 422 and 412 nm, respectively. The shifting of the peaks towards shorter wavelengths with increasing pH may be the result of decreasing dimensions of nanospheres. Photographs made by means of a transmission electron microscope confirm that all particles obtained are of spherical shape, which becomes increasingly irregular with decreasing pH. Mean diameters of silver nanospheres obtained at the pH values of 6.0, 7.0, 8.0, 9.0, 10.0 and 10.5 were equal to 73 nm, 63 nm, 56 nm, 50 nm, 40 nm and 31 nm, respectively. The scientists have also found that addition of agents that changed pH had no effect on the progress in silver reduction. What's more, the team discovered that the shape of particles approached that of perfect nanospheres, when the reaction mixture was maintained at 100°C for 2 hours. This, however, had no effect on the mean diameter of nanoparticles [37].

An interesting method of synthesizing silver nanospheres was presented by Song et al. [38]. This method does not require the use of neither surfactants nor specific solvents. Nanosilver was obtained by mixing aqueous solutions of silver nitrate (AgNO₃) and p-phenylenediamine at room temperature. By manipulating with the initial substrate concentrations, the team managed to obtain silver nanoparticles of flower-like geometry. An interesting fact was that both these structures had different wetting properties. Nanospheres proved to be exceptionally hydrophilic, whereas “nanoflowers” exhibited considerable hydrophobicity. Due to their diverse wettability, these structures can successfully be applied in microfluidizing devices and sensors. The mean diameter of the nanospheres obtained was 1.2 nm. Microscopic examinations revealed organic contamination on the surface of nanoparticles, most probably products of p-phenylenediamine oxidation. In contrast to the common knowledge that colloidal silver is unstable, the structures obtained by the Song's team proved to be considerably stable, which might be the result of a protective effect of p-phenylenediamine oxidation products [38].

**Nanodecahedrons**

Another commonly known group of silver nanoparticles are decahedrons, wherein every particle is built of ten equilateral triangles. The geometry of these particles is deemed one of the most overwhelming. Moreover, decahedral structures exhibit very interesting optical and catalytic properties, which result directly from their shape. On account of that, laboratories across the world are trying to obtain silver nanodecahedrons. The size of these particles can be adjusted by varying substrate concentrations: the lower the concentration the larger the size. Most nanodecahedrons have pentagonal cross sections. In contrast to nanocubesahedrons, decahedral particles do not have three axes of symmetry. The characteristics of an individual particle is represented by formula (1):

\[
d = \frac{1}{10} \sqrt{50 - 10\sqrt{5}}
\]

where \( l \) is the length of the edge, and \( d \) is the height of one of the two pyramids with pentagonal base making up the structure of the nanoparticle [11].

Silver nanodecahedrons were synthesized in the reaction of reducing silver nitrate (AgNO₃) with dimethylformamide in the presence of polyvinylpyrrolidone (PVP) at 140°C. The product contained a high (70%) concentration of silver particles in the form of decahedrons, the mean size of which was ca.80 nm [39]. Recent investigations indicate that silver nanodecahedrons of high purity (90%) can be synthesized by employing photoinduction. Samples obtained by this method were green in colour with a red glare. Detailed examinations have shown that nanosilver exhibited high uniformity of particles having the shape of decahedrons. Scientists have observed that the size of nanoparticles depended on the wavelength of the light. An additional advantage is that particle size can be increased by extending the time of sample irradiation. Eventually the research team obtained nanosilver in the form of decahedrons, the size of which was in the range of 35 to 120 nm.

It is suspected that decahedral particles are contained in many nanosilver products, which results from incomplete disintegration into particles of other geometry. However, the precise mechanism of nanodecahedrons formation has not been elucidated yet [11].

**Nanoicosahedrons**

Morphology of nanosilver icosahedrons is similar to that of nanodecahedron particles: the molecule is composed of twenty equilateral triangles joined by sides [11]. It was described for the first time in 1962 by Mackay, who also developed pioneering methods of synthesizing such polyhedral structures [40]. Investigations have confirmed that each nanoparticle is characterized by distinct 5-fold, 3-fold and 2-fold axes of symmetry. One of the methods of obtaining silver nanoicosahedrons is by the so-called polyol process, wherein silver nitrate (AgNO₃) dissolved in 1-amino-9-octadecan is reduced by 1,2-hexadecanediol in the presence of p-tert-butyltoluene at 200°C. Analysis of the product obtained has shown that the mean size of silver nanoparticles was 9.1 nm with a deviation of 3.6 nm. As was the case with decahedrons, the size of particles can be controlled by varying initial concentration of substrates. Investigations carried out using surface plasmon resonance indicate that silver nanoicosahedrons, with diameters ranging from 2 to 20 nm, exhibit an interesting relationship between their properties and the size of particles: with increasing size, the initially light blue peak is shifted towards deep red zone. This proves that the size of a silver nanoparticle determines its adsorptive properties [11].

There is little detailed information in the literature on nanosilver tetrahedrons, octahedrons and prisms. Research is conducted in laboratories across the world to broaden the knowledge about such nanosilver particles.

**Summary**

Synthesis of nanosilver, the particles of which assume the desired shape, is one of the major objectives of laboratory research across
the world. The ability to define reaction conditions which enable generation of nanosilver of the desired geometry is extremely important, as the properties of nanocompounds are to a great extend determined by the shape of the particles thereof. The elucidation of the morphology of nanosilver molecules is facilitated by modern instrumental techniques, such as scanning electron microscopy (SEM), or surface-enhanced Raman spectroscopy (SERS). So far, the mechanism of the generation of the various nanosilver particle shapes has not been unravelled yet. This problem, however, is now, and will in the future, constitute an important aspect of nano research.

**Literature**


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