

Plant extracts application in the process of nanosized silver preparation

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A development of methods for the preparation of nanomaterials based on biological methods is an important factor in growth nanotechnology. This group of methods includes processes that use bacteria, fungi and plant extracts. Structures components of these agents have the characteristics properties to enable carrying out the chemical reduction leading to the obtaining nanomaterials [1 ÷ 5]. With the development of nanotechnology, ecological methods have become an alternative to the traditional process, which may not always be in conformity with the principles of green chemistry and thus are not indifferent to the environment. An important feature of environmentally friendly methods is the possibility of limited need for using the substances that pose a potential threat to the environment. Additional property is the low cost of the silver ions reduction, as the process based on these methods does not require the involvement of specialized laboratory equipment [6 ÷ 10]. The fact that, as a source of silver ions is used mostly silver nitrate (V) is an opposite pole to the above-listed properties of processes using plant extracts. This substrate is obtained in synthetic way [11] and its using is not conducive to determine these methods as a totally environmentally friendly ones.

Analysing the method of preparing plant extracts, it can be assumed that the process is cumbersome and challenging for the economy of its implementation. Indeed, the selection of method leading to the extract from plant material the active substances is a key determinant of the cost of the process. However, in most publications is suggested to prepare a plant infusion, which is a form of extraction, and in which the active compounds are extracted by the flooding of the plant material with hot water. Water is the main extraction factor in the great majority of publications; organic solvents in this type of work are very rarely used.

Nanosilver is one of the most desirable nanomaterials [12 ÷ 17]. Due to its biocidal properties, this material is used in medicine, cosmetology, dental, construction, food industry and others. Nanosilver is used as an additive to the fibres in toothbrushes [18], or antibacterial soaps. [19] In the construction industry, it is a valuable action when silver nanoparticles are incorporated in the paint covering the outer surfaces, which aims to protect them against unwanted microbial growth [20]. Nanosilver valuable properties were also used in the food industry, where they are added to the working air filters such as meat processing plants [21].

This paper describes some of the methods for the preparation of nanosilver including methods involving the use of plant extracts.

Division of methods for nanosilver preparation

The rapid growth of nanotechnology and related fields has allowed for the development of a number of methods for nanosilver obtaining. Each method has a number of advantages and disadvantages related with the performance of the process, the degree of difficulty and the processing cost. Selection of a particular method has a direct impact on the quality of the resulting products such as the shape and size of the nanoparticles and their stability, the presence and orientation of the surface stabilizing molecules. The elements depending on the choice of

the synthesis could include the reaction efficiency and the amount of by-products. General methods for obtaining nanosilver division include two groups of methods: physical and chemical. Chemical methods, in contrast to physical ones, are based on the chemical reaction of Ag^+ ions to Ag^0 [22]. The group of physical methods is consists of laser ablation, a method in electric and others.

Biological processes for the silver nanoparticles production

The use of biological materials in order to obtain nanosilver is an interesting alternative to the commonly used methods. Two main streams nanosilver synthesis were developed – these are processes, which involve the use of plant material as well as those in which there are used microorganisms, such as bacteria, viruses and fungi. Is also known that there is a method in which a key role is played by the honeybee. In comparison with conventional physical or chemical processes for the preparation of nanosilver, green methods have a much greater number of benefits derived from their use. Their main advantage is the lack of impact on the environment, so these methods are in line with the principles of green chemistry. No need for synthetic reagents makes the cost of the process lower than in the case of the conventional methods. Another advantage is the ease transfer of the process on an industrial scale. Mild conditions, such as pressure and temperature not exceeding 100°C allow to classify these processes as a group of methods which are low energy- and labor-intensive. Implementation of green methods in the synthesis of nanosilver is more advantageous because keeping the bacterial culture is not required by the conditions. The resulting silver nanoparticles may be successfully applied in all areas, which are a potential target application for traditionally produced nanosilver [23]. The following describes how to carry out the synthesis using selected green plant extracts.

Gnanadesigan and colleagues [24] describe how the use of mangrove plants, which is *Rizophora mucronata*. Previous studies have shown that this plant has antibacterial and antiviral properties, which combine the desired properties of the product produced. Analysis of the leaves extract composition confirmed that there are a number of organic compounds such as alkaloids, flavonoids, polyphenols and terpenoids. The mixture of water extract and silver nitrate (V) solution was left for about 10 min, after which it was found to get brown-yellow colour, indicating the formation of silver nanoparticles. The resulting suspension was centrifuged, and the resulting precipitate was referred for further examination. UV-Vis analysis showed that the obtained suspension had a maximum absorbance at a wavelength of 420 nm, which is characteristic for nanosilver. On the basis of the atomic force microscope (AFM), it was found that most of the nanoparticles have diameters in the range of 60 to 95 nm [24].

Dwivedi and et al. [25] used an extract from the leaves of *Chenopodium album* as a factor causing the formation of nanosilver. *Chenopodium album* occurs mainly in Asia, North America and Europe. The presence of aldehydes, alkaloids, carotenoids, flavonoids and other organic substances in the *Chenopodium album* extract conducive to the formation of stable nanosilver suspensions. In addition, in the course of the teamwork it has been confirmed that the substances in the extract of *Chenopodium album* have fungicidal and antioxidant activity. The

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team claims that carbonyl groups were the factor responsible for the reduction, and carboxylic ions surrounding the silver nanoparticles acted as a stabilizing factor.

Chenopodium album leaves were obtained from the area of India. In order to obtain a nanosilver suspension, a volume of water extract of *Chenopodium album* leaves was added to solution of silver nitrate, which is a source of silver ions. After about 15 minutes, a colour changing was observed for the yellow-brown, indicating the occurrence of silver nanoparticles. It has been observed that with increasing amounts of *Chenopodium album* extract with a constant amount of silver nitrate, the colour of the resulting suspension changed from red-yellow to red. On the basis of UV-Vis it was found that the resulting amount of nanosilver is strongly dependent on the amount of extract and increases with its increase. Using TEM microscopy, it was found that the size of the resulting nanoparticles also changes with a change of the amount of extract preconceived reaction: the greater the ratio of the active substances contained in the extract to the silver nitrate was, the smaller size of silver nanoparticles were generated. TEM image analysis confirmed that in the case of high concentrations of salt, obtained particles were larger reaching 90 nm, and their amount was also significantly higher. The team observed that the time response is shortened if the silver nitrate (V) concentration is increased. Analysis of the UV-Vis spectra, carried out from time to time also provided information on the progress of the reaction over time. Characteristic peak intensity was increased nanosilver them more sample was incubated. Visible change in the position of maximum peak not been noted after incubation period equal to 2 hours. Also investigated the effect of temperature on the quality of the process the results. It was found that the peak intensity of the UV-Vis spectrum increased with the temperature of the preparation of nanoparticles. Probably, this is related to the intensification of the agglomeration process at higher temperatures. Another factor affecting the progress is the pH. The team studied the effect of pH (2 to 10) by measuring the electrokinetic potential. It turned out that the resulting suspensions were stable over a wide pH range, as demonstrated by a large absolute value of the electrokinetic potential. Furthermore, it was found that at lower pH values, suspension stability was worse, which could be explained by the fact of obtaining larger nanoparticles in a lower pH. On the basis of microscopic techniques, it was observed that the vast majority of silver nanoparticles were spherical shape and the resulting suspensions may be considered as homogeneous [25].

Bar et al [26] have described the preparation of nanosilver using the aqueous extract of *Jatropha curcas* seeds. This material consists of fats, proteins, carbohydrates and water. Fatty acids, oleic acid, linoleic acid, palmitic acid and stearic acid occur frequently. The team considers that the biomolecules, which have in their structure a carbonyl, hydroxyl and amine groups are responsible for the reduction of silver ions, and at the same time – as a molecule having a high molecular weight – for the stabilization of newly created nanoparticles. The authors clarify that latex compounds, which may be present in the *Jatropha curcas* seed extract, can be the factor preventing against nanoparticles agglomeration.

Preparation of colloidal silver suspensions consisted of mixing the extract with an aqueous silver nitrate (V) solution. After approximately 15 minutes a mixture took on the red colour, which visually shows the appearance of silver nanoparticles. This was also confirmed by UV-Vis spectroscopy, because the spectral peak maximum was located at $\lambda = 425$ nm. When the salt concentration was increased, peak maxima were shifted toward the infrared, and the corresponding absorbance value increased. This was accompanied by a colour change from yellow suspension by red to dark red one. Microscopic analysis (TEM) showed that in the case of 0.001 M silver nitrate (V) solution, formed nanoparticles had a spherical shape and their average size was included

in the range of 15 to 25 nm. For the higher concentration of salt, the nanoparticles size reached 50 nm. The team claims that suspensions obtained by this method are stable for two months, provided that they are kept in the dark [26].

Kasthuri and colleagues [27] used the leaves of *Lawsonia inermis* as a source of apiin belonging to flavonoids, which was able to reduce silver ions, because its structure contains hydroxyl and carbonyl groups. The team claims that the use of *Lawsonia inermis* leaves extract brings many economic profits, and a stable for a long time suspension are obtained. *Lawsonia inermis* leaves are known for their effectiveness in combating ulcers of the mouth, stomach, burns, swellings and pustules of smallpox. In cosmetics *Lawsonia inermis* leaves are smoothing the skin, improve circulation and skin and hair tone.

After preparation of the extract at room temperature, it was combined with the aqueous silver nitrate (V) solution and stirred. The amounts of the extract and salt were changed in each of the tests. As time went by, a colour change to dark yellow was noticed. The authors argue that such a visually prepared suspensions remained stable for the next three months. A UV-Vis study of mixture obtained by mixing the extract with silver nitrate (V) solution at different times of the progress of the reaction was performed. When time passed by, the peak maxima of the UV-Vis spectra were getting higher value, and their position was located at $\lambda = 456$ nm. TEM microscopy revealed that the obtained silver nanoparticles have a spherical shape and their average size was about 39 nm, and their distribution was homogeneous, though rare [27].

Summary

Despite the fact that the chemical and physical methods are still the main way of the nanosilver synthesis, more and more attention is paid to the biological methods, and especially those involving the use of substances contained in plant material. This is dictated by the desire to gain the knowledge about the characteristics and properties of plant materials, so that it can be used in nanotechnology processes. This direction is accompanied by a number of advantages, which include, for example, possibility to reduce the quantity of the substrates obtained synthetically. The advantage of the extraction method is limited amount of reagents used as reducing agents and a stabilizing additive, which is required in the case of the conventional method. This is ensured by the use of a single plant extract.

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Ustalenie struktur przestrzennych i mechanizmu działania metylotransferaz przez polskich naukowców

Naukowcy z Międzynarodowego Instytutu Biologii Molekularnej i Komórkowej w Warszawie (MIBMiK) we współpracy z naukowcami z Uniwersytetu Warszawskiego (UW) ustalili struktury przestrzenne i mechanizm działania białek nazywanych metylotransferazami, odpowiedzialnych za enzymatyczną biosyntezę dojrzałych cząsteczek mRNA w komórkach ludzkich. Wyniki badań zostały opublikowane w czasopiśmie *Nature Communications*.

Za pomocą krystalografii rentgenowskiej, badacze z MIBMiK określili na poziomie atomowym szczegóły kompleksu utworzonego przez w pełni funkcjonalną domenę katalityczną ludzkiej metylotransferazy kap I (CMTr1) oraz krótki fragment RNA z kapem. Otrzymanie kompleksu białka z RNA w formie odpowiedniej do badań krystalograficznych stanowiło duże wyzwanie. Bardzo trudna do uzyskania była cząsteczka RNA, która została chemicznie syntetyzowana przez grupę prof. Darżynkiewiczza na UW. Badacze z zespołu prof. Bujnickiego użyli modelu krystalograficznego

CMTr1 jako szablonu do komputerowego wymodelowania struktury analogicznego kompleksu utworzonego przez białko CMTr2 oraz cząsteczkę RNA będącą produktem reakcji katalizowanej przez CMTr1. Przeprowadzono również badania biochemiczne CMTr1 i CMTr2, aby potwierdzić znaczenie poszczególnych reszt aminokwasowych przewidzianych jako ważne dla wiązania RNA na podstawie krystalograficznych i obliczeniowych modeli strukturalnych.

„Nasze odkrycie jest przykładem udanego połączenia badań doświadczalnych i teoretycznych. Włożyliśmy w ten projekt dużo wysiłku, ale współpraca przy jego realizacji dała nam dużo satysfakcji” – mówi prof. Bujnicki w imieniu naukowców z MIBMiK. „Teraz możemy wykorzystać tę wiedzę, aby zbadać, które cząsteczki RNA w komórkach ludzkich są rozpoznawane przez CMTr1 i CMTr2, a także ukierunkować poszukiwania cząsteczek chemicznych, które zablokują działanie enzymów wirusowych, ale będą nieszkodliwe dla człowieka.” – dodaje. (kk)

(<http://biotechnologia.pl>, 9.01.2014)