Preparation of nanosilver via one-step chemical reduction in aqueous medium at elevated pressure

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Introduction

Nanosilver stands out among the newest types of bactericidal and fungicidal factors. Antibacterial and antifungal properties of nanosilver have already been confirmed in relation 650 microorganisms [1÷5]. This is due to its interaction with the thiol group located in the L-cysteine, which in turn leads to the reduction of enzymatic activity of some proteins [1, 6]. Preparations containing nanosilver are used in such areas of life as hygiene, cosmetology, prevention, care and food pasteurization [1, 6, 7].

With the spread of nanotechnology, several methods for preparation of nanomaterials were developed. Each of the methods has different process efficiency and accompanying technological limitations. Parameters of received nanoparticles, such as shape, diameter or longest dimension, stability, stabilizing agents configuration and the presence of ligands are closely related to the choice of methods leading to their receipt [6].

The paper presents a method for the preparation of silver nanostructured (nanosilver). Ascorbic acid, and gelatin were used as reducing agent of silver ions and stabilizing factor, respectively [9].

Ascorbic acid has antioxidant properties. It plays an important role in the functioning of the human body. It affects the production and maintenance of collagen, promotes healing of wounds, prevents hemorrhage and increased resistance to infection and disease. It is used in the food industry as a food additive and in pharmaceuticals as well [9].

Gelatin is a natural substance, whose dry weight in 98–99 % is consisted of a mixture of proteins and peptides. Glycine, proline and hydroxyproline belong to amino acids which are gelatin basic building blocks. What is more, gelatin contains such amino acids as: glutamic acid, alanine, aspartic acid, lysine, serine, leucine, valine, phenylalanine, threonine, isoleucine, hydroxylysine, histidine, methionine, and a little amount of tyrosine. An interesting feature of gelatine is its local antihemorrhagical action. The principle of local bleeding haemostasis involves the destruction of the surface platelets, which leads to the coagulation process. Gelatin is also considered as a substance improving the overall health condition. Studies have confirmed that gelatin has a soothing effect on knee pain and reduces stiffness. Gelatin is also used as a drug that prevents and treats the hypotension and hypovolaemia. This drug is also used in the treatment of haemodilution. In the food industry gelatine serves as a food additive denoted with E441 symbol. In 1993, the U.S. Food and Drug Administration gave gelatin status as a substance which is Generally Regarded As Safe (GRAS), and it was found that there is no contraindication to use it anywhere regardless of the source and origin country [9].

The use of biocompatible materials in the preparation of nanosilver is particularly important because of the possibility to use it in medicine, dentistry, pharmacy, cosmetics, etc. Furthermore a reducer and a stabilizer are non-toxic and harmless to the environment. Ecological indifference of these chemicals puts the method as environmentally friendly one and at the same time causes that the methodology is in the line of green chemistry principles.

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Experimental part

The chemical synthesis in an aqueous medium was used in order to obtain nanosilver. As a source of silver ions, silver nitrate was used (analytically pure) and gelatin (analytically pure) served as a stabilizer. L(+)-ascorbic acid (analytically pure) was used as a reducing agent. The process was conducted in 4525 PARR pressure reactor [10].

To an aqueous solution of $AgNO_3$ (100 cm^3, 0.001 mol/dm^3) an aqueous gelatin solution (50 cm^3) was added. The solution was heated in the reactor to a temperature of 110–150°C. After required temperature was reached the mixture was fed with an aqueous solution of ascorbic acid (50 cm^3) using a pump. The reduction reaction was carried out during 2–30 min [10]. The process parameters are summarized in Table 1.

Table 1

Process parameters of nanosilver receiving

System no.	Gelatin mass, g	Molar ratio $C_6H_8O_6$:Ag^+	Process temperature, °C	Reaction time, min	Pressure, Pa	Average size of nanoparticles, nm
1	0.1	3.0	110	2	0	40.2
2	0.2	3.0	130	30	138000	8.2
3	0.3	5.5	130	2	138000	5.1
4	0.3	3.0	150	16	345000	123.4
5	0.2	5.5	130	16	138000	48.7

After autoclaving colorless solution of silver nitrate, gelatin and ascorbic acid became brown, indicating the creation of silver nanoparticles. After cooling, the resulting suspensions were analyzed.

Spectrophotometric study of nanosilver suspensions was performed using UV1800 Rayleigh spectrophotometer. The average size and nanoparticles fractional distribution was determined by DLS technique using a Malvern Nano ZS Setasizer. Assessment of nanoparticles morphology was done on the basis of images obtained by atomic force microscopy AFM on Veeco Company (USA) NanoScope V.

Results discussion

The derived UV-Vis absorption spectra of nanosilver suspension are shown in Figure 1. Peak at 400–450 nm corresponds to surface plasmon resonance characteristic for silver nanoparticles. Surface plasmons are compatible oscillations of valence electrons located on the material surface atoms.

The absorption of radiation by metal nanoparticles depends essentially on their size and shape. Plasmons are not symmetrical, which means that the solutions contain aggregated particles. This is confirmed by photomicrographs obtain on atomic force microscope shown in Figure 2. The resulting UV-Vis absorption bands are rightward (with absorbance tail at longer wavelength), which may result from the nanoparticle size distribution presented in Figure 3. The intensity of plasmon resonance is in fact dependent on the size of the particles aggregates and thus the relationship between the amount of particles and the absorbance intensity is not linear. Furthermore, if the particles are not spherical and have a shape similar to an ellipsoid, the absorption line associated with surface plasmons is divided into two branches associated with the perpendicular and parallel to the long axis of the ellipse oscillations. It is visible in the absorption spectra of the systems no. 1, 3 and 5 (Fig. 1).

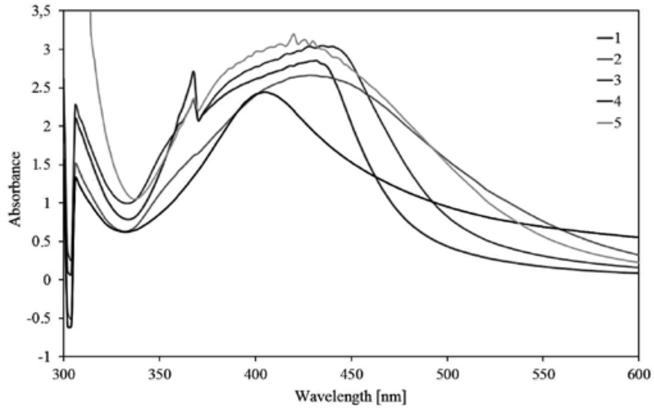

Fig. 1. The absorption spectra of silver nanoparticles

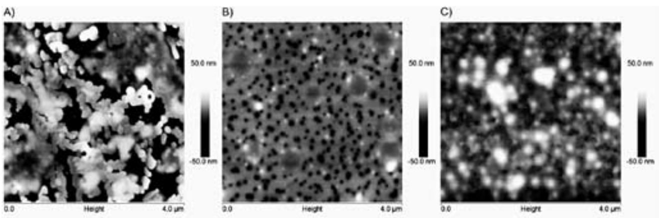

Fig. 2. AFM microphotographs of silver nanoparticles: A) system 1; B) system 2; C) system 5

Basing on the obtained results it can be concluded that the time extension does not affect the autoclaving process to obtain nanosilver. Under the process conditions there hasn't been observed any effect of ascorbic acid concentration on the size of obtained nanoparticles.

At elevated temperatures, gelatin is soluble in water. In the aquatic environment bonding between collagen fibers break, peptide chains are displaced to form a colloidal system for obtaining the silver nanostructured. However, a significant increase in temperature and the resulting pressure rise, intensifies process of peptides grouping in larger agglomerates, which reduces the stabilization of silver nanoparticles, and it effects on their size. With the rise in temperature the average size of the nanoparticles increases.

Increasing the gelatin solution concentration enhances the stability of nanoparticles allowing to obtain smaller particles.

Conclusion

Nanosilver synthesis was carried by a one-step chemical reduction. Environmentally friendly reducing and stabilizing agents were used. Ease of the process conduction, its controlling, the ability to adjust the size of nanoparticles and to obtain monodisperse suspension is the important advantage of the method.

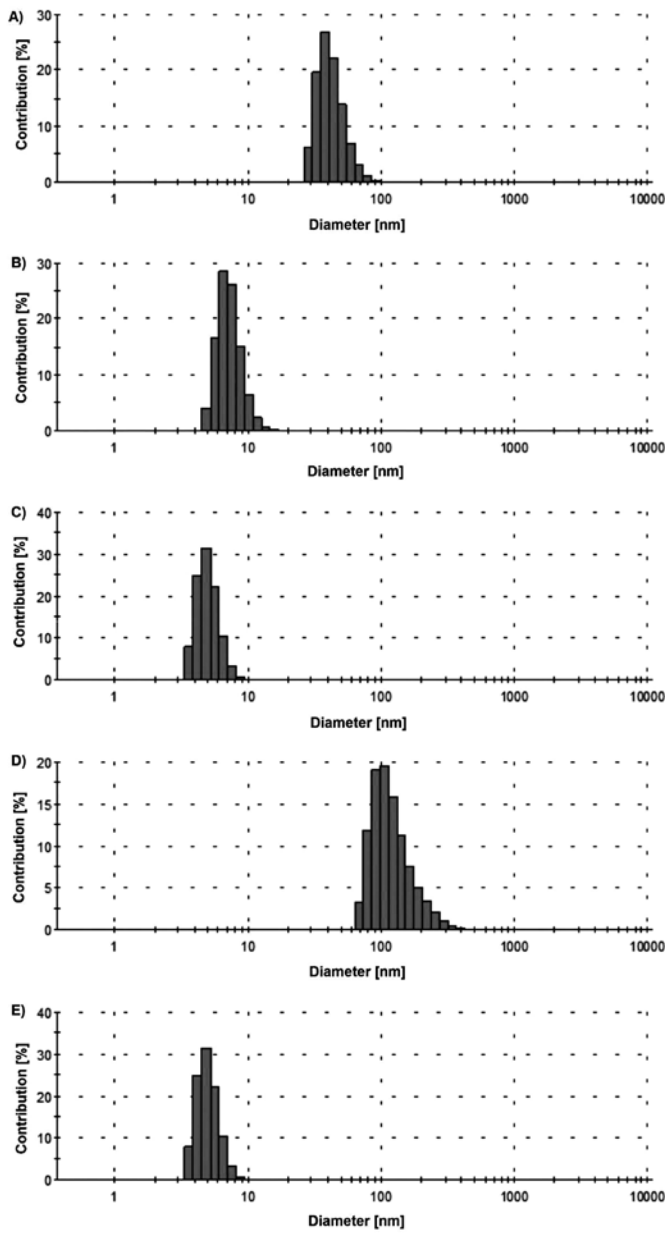

Fig. 3. The size distribution of silver nanoparticles: A) system 1; B) system 2; C) system 3; D) system 4; E) system 5

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KONKURSY, NAGRODY

Spółki Grupy Azoty – Diamentami 2014

Wchodzące w skład Grupy Azoty spółki: Grupa Azoty ZA Puławy i Grupa Azoty Automatyka zostały laureatami „Diamentów Forbesa".

„Diamenty Forbesa" to firmy, rentowne (na podstawie wskaźników EBIT i ROA), z wysoką płynnością bieżącą i nie zalegajce z płatnościami. Ponadto wykazują się dodatnim wynikiem finansowym oraz wartością kapitałów własnych.

Na liście „Diamentów" znalazły się przedsiębiorstwa, które osiągnęły największy przeciętny roczny wzrost wartości. Oceniane były na podstawie sprawozdań finansowych złożonych do KRS. Dodatkowo została sprawdzona geneza wyniku laureatów w celu wyeliminowania przedsiębiorstw, w których skokowy wzrost wartości był efektem jednorazowych zdarzeń nadzwyczajnych. Pod uwagę brane były wyniki z lat 2010–2012.

Puławska spółka zajęła w tym zestawieniu wysokie 18. miejsce w skali kraju i pierwsze w województwie lubelskim. Grupa Azoty ZA Puławy uzyskała nagrodę w kategorii firm dużych, czyli o przychodach powyżej 250 mln PLN. Z kolei Grupa Azoty Automatyka, mająca swoją siedzibę w Tarnowie, ulokowała się na 3. miejscu w rankingu małopolskim (11. miejscu na liście ogólnokrajowej) w kategorii przedsiębiorstw średnich, tj. o przychodach od 50 do 250 mln PLN. *(em)*

(http://grupaazoty.com/pl/wydarzenia/469 6.02.2014 r.)

Kolejne mamy-badaczki nagrodzone w programie Pomost

15 mam–badaczek nagrodziła Fundacja na rzecz Nauki Polskiej (FNP) w ósmej i ostatniej edycji programu „Pomost". Uczone, które wracają do pracy po przerwie związanej z opieką nad dzieckiem, otrzymają w sumie blisko 4 mln zł. Laureatki będą prowadzić badania w dziedzinach Bio, Info, Techno.

Najwyższe dofinansowanie – ponad 268 tys. PLN. – przyznano dr Magdalenie Czeredys z Międzynarodowego Instytutu Biologii Molekularnej i Komórkowej w Warszawie. Po 268 tys. PLN otrzymały: dr Katarzyna Arczewska z Centrum Medycznego Kształcenia Podyplomowego w Warszawie; dr Karolina Bukowska-Strakova z Uniwersytetu Jagiellońskiego – Collegium Medicum, dr Joanna Chwiej z Akademii Górniczo-Hutniczej im. Stanisława Staszica w Krakowie, dr Mariola Dutkiewicz z Instytutu Chemii Bioorganicznej PAN w Poznaniu, dr Marta Kolasa z Uniwersytetu Technologiczno-Przyrodniczego im. Jana i Jędrzeja Śniadeckich w Bydgoszczy, dr hab. Katarzyna Koziak z Warszawskiego Uniwersytetu Medycznego, dr Julita Smalc-Koziorowska z Instytutu Wysokich Ciśnień PAN w Warszawie. *(em)*

(http://www.naukawpolsce.pap.pl/aktualnosci/news,399111,kolejne-mamy--badaczki-nagrodzone-w-programie-pomost.html 16 luty 2014 r.)

AKTUALNOŚCI BIOTECHNOLOGICZNE

Audi inwestuje w biopaliwa

Producent samochodów marki Audi postanowił ponownie zainwestować w rozwój technologii związanych z biopaliwami. Ogłoszono decyzję o współpracy Audi z francuską firmą biotechnologiczną Global Bioenergies. Celem wspólnego projektu będzie strategiczne partnerstwo obu stron w rozwoju technologii biopaliwowej, opartej na stosowaniu izooktanu w silnikach benzynowych. Jest to kolejny już krok producenta samochodów w kierunku rozwoju możliwości wykorzystania paliw niekopalnych.

Global Bioenergies to francuska firma specjalizująca się w wytwarzaniu lekkich olefin w procesach biotechnologicznych. Jedną z biotechnologicznie pozyskiwanych olefin jest izobuten, który następnie może zostać przekształcony w izooktan – wysokiej jakości paliwo, o najwyższej możliwej liczbie oktanowej. Innowacyjne paliwo, w którym nadzieje inwestycyjne pokłada firma Audi, to właśnie pochodne izooktanu otrzymywanego z bio-izobutenu. Izooktan, w tym przypadku uzyskiwany z wykorzystaniem źródeł odnawialnych, może być skutecznie łączony z konwencjonalnymi paliwami do silników benzynowych, w dowolnym stosunku ilościowym.

Współpraca z Global Bioenergies przy opracowywaniu nowych biobenzyn to kolejne działanie firmy Audi na rzecz rozwoju możliwości wykorzystania biopaliw, obok projektów dotyczących biogazu i biodiesla.

http://bio-based.eu/news/global-bioenergies-audi-partner-drop-biofuel/27.01.2014

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