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GREEN SYNTHESIS OF IRREGULARLY SHAPED GOLD NANOPARTICLES

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Abstract: The synthesis and application of new nanomaterials have become a key technology for many fields, like electronics, engineering, optics, computer science, sensorics, and biomedicine. Therefore, there is an interest to new cost, energy, and time effective methods for preparation of new nanomaterials.

Biomedical application of nanomaterials is limited not only by control over the size and morphology of nanoparticles but also by their biocompatibility. However, the trusted protocols normally involve the application of reducing agents (sodium borohydride, methoxy polyethylene glycol, potassium tartrate, etc.) and capping agents (sodium dodecyl benzyl sulphate, polyvinyl-pyrrolidone, etc.) which are usually toxic. The unavoidable presence of toxic compounds in nanocolloid systems limits the applications of the nanoparticles for biological systems.

The aim of this study is the analysis of recent reports and evaluation of perspectives for the development of green methods of metal nanoparticles for biomedical applications.

Numerous physical-chemical methods are in use for the characterization of nanoparticles: ultraviolet and visible spectroscopy for characterization of surface plasmon resonance, infrared spectroscopy for characterization of capping agents, surface and transmission electron microscopy and atomic force microscopy for size and shape studies, energy-dispersive X-ray spectroscopy for chemical composition determination and dynamic light scattering for size determination.

Analysis of recent studies have shown that the extracts of selected plants (juniper, goldenrod, spearmint, lemon balm etc.) can be successfully used for preparation of biocompatible plasmonic materials with response in infrared region what make them attractive for biomedical applications.

Keywords: nanomaterials, nanoparticles, phytosynthesis, plasmonic materials, spectroscopy

INTRODUCTION

Nanomaterials have become an important branch of modern science due to the unique physical and chemical properties. Due to their unusual electric, optical, magnetic, and catalytic properties, nanomaterials were recognised as a new and efficient method for the creation of novel advanced materials.

Biocompatibility and optical properties (surface plasmon resonance) of noble metals nanoparticles open the possibility of its modern applications in nanomedicine, which is currently being actively developed. Nanoparticles of noble metals are employed to deliver therapeutics and mediate heat and light to specific types of tissues [1]. The composition, structure, size, shape, and of metal nanoparticles define the optical and electronic properties which can be adjusted to utilisation for advanced photothermal therapy [2] and the controlled drug release systems [3].

Gold nanoparticles with their excellent chemical stability and biocompatibility are suitable for biomedical applications. However, gold nanoparticles with reasonably small size (< 60 nm) exhibit their surface plasmon resonance in the range of 510-560 nm, i.e., far beyond the biological transparency window of 650-1350 nm. This region is divided into two optical near-infrared ranges, at $\lambda = 650-850$ nm and 950-1350 nm, respectively. The effective utilisation of nanoparticles for photothermal therapy because of the deeper penetration of long-wave radiation requires nanoparticles with response in the second near infrared range [4]. By this reason, the significant interest of scientist is dedicated to the synthesis of gold nanoparticles with regular (spherical) and irregular shapes (non-spherical) – spherical [5, 6], nanorods [7], nanoshells [8], nanostars [9], nanoprisms [10], nanotriangles [11, 12], and nanohexagons [13].

Numerous syntheses methods for the synthesis of metal nanoparticles were developed in recent decades: hydrothermal synthesis, coprecipitation, microemulsion, inert gas condensation, ion sputtering scattering, microwave, pulse laser ablation, sol-gel, spark discharge, sonochemical, and biological synthesis. Physical methods usually require the utilisation of highly expensive equipment and do not provide the control over parameters of final nanoparticles (size and shape). Therefore, traditional wet chemistry methods were recognised as more preferable. However, there is often a need to use toxic reducing and capping agents which stay in resulting nanocolloids. As result, such nanoparticles show high cytotoxicity towards living organisms and are unsuitable for application in biomedicine.

Biological methods of nanoparticles synthesis which are consist in the application of biological materials (plants, fungi and bacteria), can be considered as a possible alternative. Such methods are also cost- and time-effective and environmentally friendly. One of the routes for obtaining biocompatible non-spherical gold nanoparticles in the greenest manner is phytosynthesis - the using of plant extracts and natural surfactants [14].

Despite the extensive studies, the wide application of photosynthetic protocols is restricted due to many components presented in the plant extracts and the limited knowledge on the formation mechanism of non-spherical nanoparticles [15].

This study aims to consider the recent state in the development of the phytosynthesis protocols for preparation of gold nanoparticles with optical activity in the near infrared region.

MATERIALS AND METHODS

Chemicals

Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 96% p.a., ITES Vranov, Slovak Republic (SR)) and acetic acid (CH_3COOH , 99% p.a., Centralchem, SR) were used for extraction of the plant material. Sodium hydroxide (NaOH) 0.1 mol/L standard solution (Normanal, Lach-Ner, s.r.o., CR), silver nitrate (AgNO_3 , ITES Vranov, SR) and chloroauric acid hydrate ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$, Sigma-Aldrich, St. Louis, MO, USA) were used for nanoparticle synthesis. Double-distilled water was used for extract preparation, reagents preparation and nanoparticles synthesis.

Synthesis of nanoparticles

Aqueous and aqueous-ethanol leaves extracts of juniper (*Juniperus communis*) [11], peppermint (*Mentha piperita*) [12], and goldenrod (*Solidago canadensis*) [13] were applied for the synthesis of gold nanoparticles. Syntheses were performed at an ambient laboratory temperature (20-25 °C), by the direct interaction of the plant extracts with 1 mM HAuCl_4 aqueous solution under continuous stirring. Amounts of extracts were normalized to dry matter content, with the estimation of 0.25-1.5 mg/ml of the dry matter in the final solution. In a typical synthesis, the estimated volume of plant extract was diluted by double distilled water followed by addition of 1 mM HAuCl_4 solution.

Aqueous and aqueous-ethanol extracts of elderberry fruits (*Sambucus nigra*) [6] were used for preparation of silver nanoparticles by direct interaction of extract with 1-10 mM AgNO_3 at 55°C for 24 hours. The pH of reaction mixture was adjusted with NaOH solution.

Characterization of nanoparticles

UV-Vis spectra were collected by Shimadzu UV-1800 spectrophotometer with matched 1-cm quartz cells. Attenuated total reflectance Fourier transform infrared spectra were acquired with a Shimadzu Prestige 21 instrument equipped with a single reflection accessory and ZnSe ATR crystal (PIKE Technologies, USA). Transmission electron microscopy imaging was conducted with a JEOL JEM-2100F microscope equipped with attachments for electron-dispersive X-ray analysis and a GIF TRIDIEM post-column energy filter for the acquisition of energy-filtered images and selected area electron diffraction. TEM specimens were prepared by dropping a sonicated aqueous suspension of AuNPs on a carbon-coated copper grid and followed with drying it under the infrared lamp. Transmission electron images of different magnifications were captured at a maximum acceleration voltage of 200 kV. A selected nanometer-sized object was imaged by atomic force microscopy with a commercial Nanoscope III instrument (Digital Instruments, Santa Barbara, CA).

RESULTS AND DISCUSSION

UV-Vis spectroscopy was applied to follow the nanoparticles formation through the observation of the position and shape of surface plasmon resonance peaks (Fig. 1). The spectrum of silver nanoparticles prepared with elderberry extract contains the single surface plasmon resonance peaks at 395 nm which confirm the formation of spherical nanoparticles. However, the spectra of gold nanoparticles prepared using different extracts are different. In some cases, the second maximum in the near infrared range occurs. For example, some extracts (clove [5], elderberry [6]) produce spherical nanoparticles (Figure 1, red). But others, support the formation of both spherical [11], peppermint [12], and goldenrod [13]) and non-spherical nanoparticles (blue). The occurrence of absorbance in the near infrared range depends not only on the selected extract, but also on the extract to Au^{3+} ions ratio. Usually, low concentrations of Au^{3+} ions are lead to the formation of spherical nanoparticles. The absorbance in the near infrared range increases with the concentration of reagents. But only to a certain limit when the formation of macroparticles occurs.

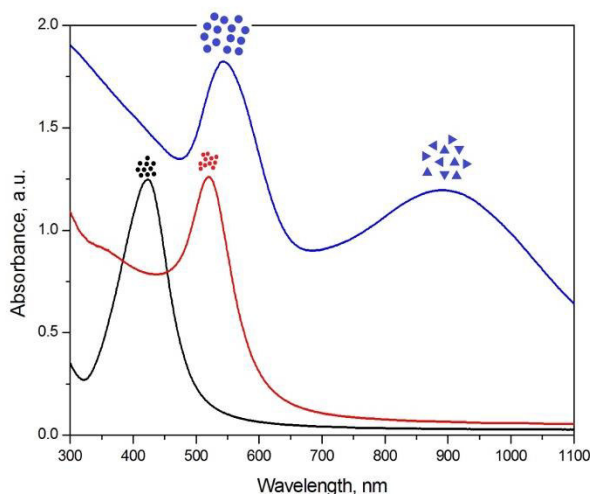


Figure (1): UV-Vis spectra of silver (black), spherical gold (red) and non-spherical (blue) gold nanoparticles prepared using plant extracts.

A simultaneous presence of highly monodisperse spherical silver (Figure 2a) and gold (Figure 2b) nanoparticles with diameter of 10 nm in nanocolloid solution are confirmed by transmission electron microscopy. As can be seen from the typical transmission electron microscopy image (Figure 2c), the average composition of gold nanocolloids shows the presence of triangular and pseudospherical particles in the nano-dimensions.

Energy dispersive X-ray analysis confirmed that the resulting morphological different nanoparticles are all gold nanoparticles (Figure 3). The smallest nanotriangles have 20–50-nm edge lengths. Above-mentioned studies confirm the high polydispersity of nanoparticles. Phytosynthesised nanocolloids contain nanoparticles with different sizes regardless of the intensity of stirring during the preparation. This might be solved by fractionalisation of extract before the synthesis of nanoparticles. However, we need to learn the role of different components of extract more. With this aim, the transformation of organic compounds in a reaction mixture was followed by Fourier transform infrared spectroscopy. The comparison of spectra [6, 11] suggests that reduction of Au^{3+} is followed with the oxidation of polyphenolic hydroxyl groups to carbonyl groups which play an important role in the stabilisation of nanoparticles.

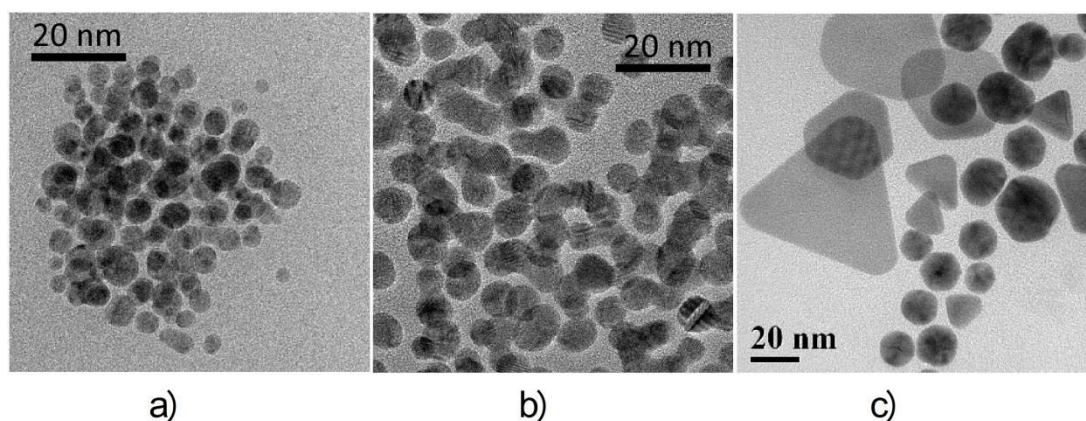


Figure (2): Transmission electron images of phytosynthesized a) silver, b) spherical gold and c) non-spherical gold nanoparticles.

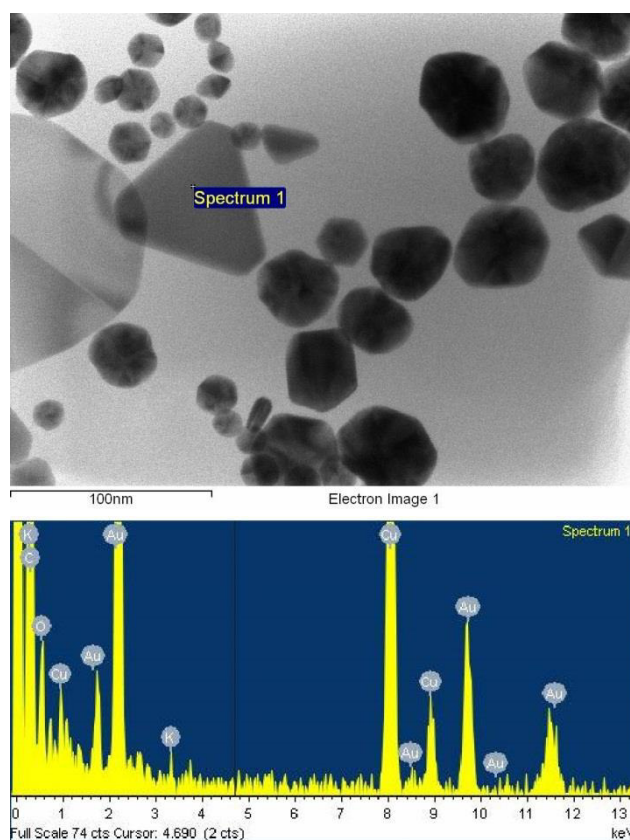


Figure (3): Transmission electron image (upper) and energy dispersive X-ray analysis (down) for gold nanoparticles prepared with goldenrod extract.

Other alternative for preparation of monodisperse irregular shape gold nanoparticles is further separation by centrifugation or electrophoresis.

CONCLUSIONS

The easy green protocols for synthesis of spherical silver and gold nanoparticles and irregular shaped gold nanoparticles are considered. It was observed that the utilisation of some plant extracts (*Syzygium aromaticum* L., *Sambucus nigra*) leads to the formation of almost perfectly spherical silver and gold nanoparticles. However, the application of the different ratios of the other aqueous and aqueous-ethanol plant extracts, like *Juniperus communis*, *Solidago canadensis*, *Mentha × piperita*, leads to preparation of the prismatic-shaped gold nanoparticles.

It was observed that the using of extracts of selected plants as reducing and capping agents lead to the formation of both spherical and non-spherical nanoparticles. The ratio between reagents (extract to Au^{3+} ions) can influence the ration of different shaped nanoparticles.

Fourier transform infrared spectroscopy analysis proves the presence of hydroxyl, carbonyl, and carboxyl groups on the surface of metallic nanoparticles. Increasing absorbance of the carbonyl bonds in the infrared spectra of nanoparticles confirms the significant role of polyphenols of the plant extracts in the self-organization and stabilization of metal nanoparticles.

The synthesis of nanoparticles is a prospective route for green preparation of biocompatible nanoparticles for biomedical applications, but there are still many questions which need to be answered.

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