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Synthesis, properties and functionalization of gold nanostars for medical diagnostics

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The aim of the research. To evaluate two approaches to colloidal synthesis using two different non-toxic surfactants (PVP and Triton X-100) and their properties for future use.

Material and methods. (PVP) The solution of GNSs with short tips was prepared in 200 ml vial. 20 mg of PVP (Polyvinylpyrrolidone, 1-ethenylpyrrolidin-2-one) were dissolved in the 200 mL of DMF (N,N-Dimethylmethanamide) (with the sonication to dissolve well). (Triton X-100) In a typical preparation of GNSs with long tips, the seed solution was prepared in a 20mL vial: 5mL of HAuCl4 5·10-4M in water are added to 5mL of an aqueous solution of TritonX-100 0.1M. To examinate the shape and properties of prepared gold nanostars Cary 100 Bio Spectrophotometer using quartz cuvettes was used to taken on UV-Vis spectra. Transmission Electron Microscopy (TEM) was used to obtain shape and size of prepared GNSs.

Results. Microscopy analysis shows that the obtained GNSs have completely different shapes. The GNSs fabricated using synthesis approach with PVP have shorter tips and the cores are larger than the GNSs synthesized with Triton X-100 synthesis approach. TEM-images of the second ones show smaller size nanoparticles with the longer and thinner tips. Optical properties of the synthesized GNSs were analyzed using UV-vis-NIR absorbtion spectra, which shows maximum plasmon existence at 800 nm for GNSs synthesized with PVP and at 850 nm for GNSs synthesized with Triton X-100.

Conclusion. In summary, we developed GNSs using two colloidal synthesis approaches with the use of two different non-toxic surfactants (PVP and Triton X-100). In the future, gold nanostars are planned to be used to develop highly sensitive methods of medical diagnostics.

Key words: colloidal synthesis, gold nanostars, absorbtion spectra.

Conflict of interest. The authors declare the absence of obvious and potential conflicts of interest associated with the publication of this article.

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Introduction

Gold nanoparticles exhibit strong localized surface plasmon resonances (LSPR) [1], which are associated with collective oscillations of conduction electrons that arise when the metal interacts with visible or near-infrared light. These resonances strongly depend on the shape, size and composition of particles, as well as on the dielectric properties of the metal itself and the environment [2]. Such customizability and sensitivity have stimulated the development of new synthetic strategies for controlling the shape of particles [3], which, in turn, allow us to anticipate the implementation of a number of potential applications in various fields, such as electronics [4], photonics. [5] or biosensors [6]. In some of these applications, in particular, in the so-called LSPR biosensor [7], the sensitivity of nanoparticles to changes in the local dielectric medium is an important parameter that should be taken into account. Since the sensitivity is determined by the degree of limitation of plasmon oscillations, which are responsible for the amplification of the near electric field at the particle surface, anisotropic metal nanoparticles such as rods, bipyramids, or stars have been identified as interesting systems. Gold nanostars (GNSs) are especially interesting because their intrinsic properties are the result of hybridization of plasmons concentrated in the core and tips of the nanoparticles. The core acts as an antenna that amplifies the electromagnetic field of the residual plasmons [8], and the morphology of the spikes (length or opening angle) and their number also have a strong influence on the frequency and intensity of plasmons. Here we report about two colloidal synthesis approaches with the use of two different non-toxic surfactants (PVP and Triton X-100) and their properties for future application.

Material and methods

(PVP) The solution of GNSs with short tips was prepared in 200 ml vial. 20 mg of PVP (Polyvinylpyrrolidone, 1-ethenylpyrrolidin-2-one) were dissolved in the 200 mL of DMF (N,N-Dimethylmethanamide) (with the sonication to dissolve well). Then the stirring plate with magnet was used for good dissolving of the following materials. 1093 μL of the $HAuCl_4$ 50 mM were added to the solution and after 8 min the 150 μL of the 15nm Au seeds were added to the stirring solution, after approximately

10 min the color of the solution went from 'transparent' to dark blue. The solution was left stirring for 24 h. And then the content was divided into 4 vials of 50 mL and washed.

(Triton X-100) In a typical preparation of GNSs with long tips, the seed solution was prepared in a 20mL vial: 5mL of $HAuCl_4$ $5 \cdot 10^{-4}$M in water are added to 5mL of an aqueous solution of TritonX-100 0.1M. The mixture is gently hand-shaken and a pale-yellow color is obtained. Then, 0.6mL of a previously ice-cooled solution of $NaBH_4$ 0.01M in water are added. The mixture is gently hand-shaken and a reddish-brown color appears. The seed solution is kept in ice and used in few hours (2 hours). The growth solution was prepared in a 20mL vial, 250μL of $AgNO_3$ 0.004M in water, 5mL of $HAuCl_4$ 0.001M in water are added in this order to 5mL of an aqueous solution of TritonX-100 0.2M. Then, a 140-400μL volume of an aqueous solution of ascorbic acid 0.0788M are added. The solution, after gentle mixing, becomes colorless. Soon after, 12μL of the seed solution are added. The solution is gently hand-shaken and a grey color appears and quickly changes to green and becomes more intense. The sample is allowed to equilibrate for 1h at room temperature and then washed.

All the glassware used for seedgrowth methods was always pretreated before use. It was washed in aqua regia for 24 hours to remove Au seeds, then washed and filled with bidistilled water.

To examinate the shape and properties of prepared gold nanostars Cary 100 Bio Spectrophotometer using quartz cuvettes was used to taken on UV-Vis spectra. Centrifugation was carried out using the Universal 320 centrifuge (Hettich Zentrifugen) and Sorvall Legend Micro 21R centrifuge with the use of polypropylene 50mL tubes. The centrifugation speed was in the 5000-4500 rpm range.

Transmission Electron Microscopy (TEM) was used to obtain shape and size of prepared GNSs. Solutions of GNSs (10 μL) were deposited on copper grids (400 mesh) covered with a carbon film. Images were taken using TEM Jeol JEM 2010.

Results

Microscopy analysis shows that the obtained GNSs have completely different shapes. The GNSs fabricated using synthesis approach with PVP have shorter tips and the cores are larger (Fig. 1(A)) than the GNSs synthesized with Triton X-100 synthesis approach. TEM-images of the second ones show smaller size nanoparticles with the longer and thinner tips (Fig. 1(B)).

Optical properties of the synthesized GNSs were analyzed using UV-vis-NIR absorbtion spectra (Fig. 2), which shows maximum plasmon existence at 800 nm for GNSs synthesized with PVP and at 850 nm for GNSs synthesized with Triton X-100.

Conclusion

In summary, we developed GNSs using two colloidal synthesis approaches with the use of two different non-toxic surfactants (PVP and Triton X-100). The results of the synthesis show that the have optical properties of synthesized nanoparticles are suitable for development of LSPR-biosensors and medicine applications such as be used as a photothermal material for the hyperthermic destruction of cancer using NIR light. In the future, gold nanostars are planned to be used to develop highly sensitive methods of medical diagnostics.

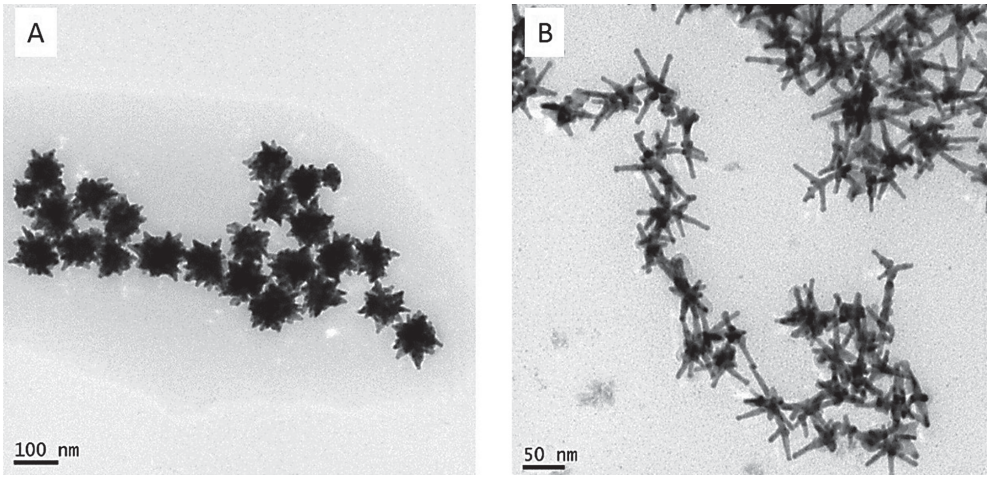

Figure 1. TEM-images of GNSs synthesized with (A) synthesis approach with PVP, (B) synthesis approach with Triton X-100.

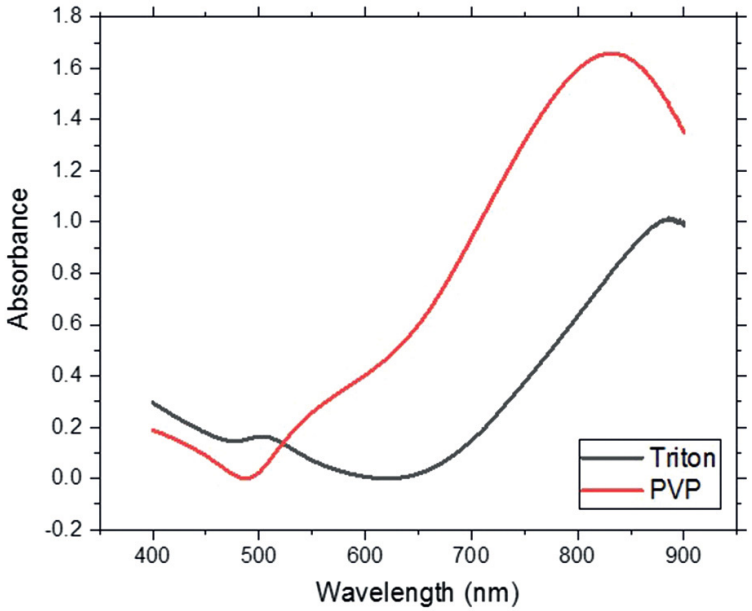

Figure 2. UV-vis-NIR absorption spectra obtained for GNSs synthesized with PVP and Triton X-100 surfactants.

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