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SYNTHESIS OF SILVER NANOPARTICLES IN DIFFERENT POLYMERS ENVIRONMENT

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Synthesis and stabilization of silver nanoparticles in different reaction conditions have been carried out with gum arabic with an average molecular weight of 200 kDa and 40000 of polyethylene glycol, as well as in 200 kDa chitosan (Cht) condition in the presence of small concentration of $NaBH_4$ and HCOOH aqueous solutions at 293–353 K temperature. The sizes of obtained silver nanoparticles were investiqated by X-ray phase analysis. It was determined that the size of silver nanoparticles stabilized in polyethylene glycol and gum arabic based co-polymers conditions range between 7–9 nm, while the sizes of formed silver nanoparticles range between 8–11 nm when using Cht being natural polysaccharide as the stabilizer.

Keywords: *silver nanoparticles, gum arabic, chitosan, polyethylene glycol, nanocomposites, XRD-ray.*

Introduction

Recently, studying synthesis, structure, and properties of Cu, Au, Ag, Pt and Pd nanoparticles containing polymer compositions has been the main directions of a scientific community. High optical [1, 2], catalytic [2, 3], conductive [4, 5] and medical [6–8] properties of polymer materials containing metal nanoparticles make their research and a wide range of synthesis more urgent. Sizes of metal nanoparticles in nanocomposites define their direct application areas.

Usage of synthetic polymers containing polar functional groups as a stabilizing agent in these researches, preparation of silver nanoparticles, studying their structures and properties are in the focus of interest [9–14]. It is possible to regulate sizes of metal nanoparticles depending on nature of selected stabilizing and reducing agent and process condition. It is known that depending on particle size polymer composites containing silver nanoparticles are widely used in medicine as a carrier for immobilization of bionanocomposites, bionanocatalysts, antibacterial preparations and biologically active compounds [15–20].

The use of some biopolymers as stabilizing agent and different type reducers provides wider effects of obtained nanocomposite. High therapy opportunities and antimicrobial properties of silver nanoparticles were studied by researchers. In some works the use of Ag^0 nanoparticles in the treatment of cancer was studied [21]. But the shortcoming is that when using >20 nm of Ag^0 nanoparticles freely the healthy cells are also exposed to toxic effects.

In other work, we synthesized 25 nm of silver nanoparticles by using aniline as a reducer and showed their application in the preparation of different preparations [22].

Priya and his colleagues have used *Musa balbisiana* (banana), *Azadirachta indica* (neem) and *Ocimum tenuiflorum* (black tulsi) extracts and carried out ″green synthesis″ of silver nanoparticles. Antibacterial and toxic properties of 20–25 nm of silver nanoextractants showed positive results [23].

<10 nm of Ag^0 and Au^0 nanoparticles were prepared by using poly-N-vinylpyrrolidone as both reducer and stabilizer [24]. Synthesized nanocomposites were used in the production of optical and magnetic materials.

In the present work, we synthesized Ag^0 by polyethyleneglycol (PEG), gum arabic (GA) and chitosan (Cht).

Experimental part

Materials. GA with average molecular weigth of 200 kDa used as a stabilizer has 97% chemical purity. Chitosan with 84% deacetylation degree and average molecular weight of 200 kDa was purchased from Sigma-Aldrich. Average molecular weight of 97% chemically pure PEG is

40 kDa and was purchased from Fluka. Both polymers were used without purification in experiments. As silver precursor $AgNO_3$ (99.98%) from Mersk (Germany) was taken. All the chemical reagents – natrium boron hydrate 98% ($NaBH_4$), acetic acid (CH_3COOH), formic acid (HCOOH), deionized water and precipitants are chemically pure and from Fluka.

Synthesis of Ag colloidal. PEG and GA are dissolved in 2:1 mass ratio in 100 ml of deionized water within 2 h, 0.5 g Cht is dissolved in 25 ml of acetic acid by mixing 15 min and 5 ml of 2.5×10^{-2} M $AgNO_3$ is added to the solution and mixed at room temperature for 2 h. Then in two parallel experiments, $NaBH_4$ and HCOOH with relevant concentrations are added into the solution and mixed at 293 K. After 15–20 min color of the solution changes from yellow to dark brown and black. The solution is deposited at diethyl ether or acetone, dried after washing 2–3 times with ethanol and brought into constant mass under atmospheric pressure. To study the impact of different factors on sizes of nanoparticles the reduction process was conducted at 293, 313, 333, 353 K temperatures, in m(PEG):m(GA)=1:1, 1:2, 2:1, as well as (Cht):m($AgNO_3$) mass ratios, in 5, 10, 20, 30 and 60 min intervals.

Results and Discussion

In experiments PEG and biologically active natural polysaccharide GA are separately used as a soluble unique polymer matrix in the stabilization of metal nanoparticles. It is known that PEG with $H(OCH_2CH_2)_nOH$ formula is soluble in water and is widely used in pharmacology and cosmetic industry. Natural polysaccharide GA contains –OH and –COOH groups and has wide application areas as an immunomodulator, gastroprotector, antioxidant and carrier in medicine and biotechnology. We compared the reduction of Ag^+ ions with $NaBH_4$ and HCOOH and investigated the dimensions of nanoparticles and use of them for biological purposes. It was shown that PEG and GA macromolecules form a homogeneous system at aqueous medium and their functional groups create a configuration with each other in more favourable form. Ag^+ ions are coordinated around –OH and –COOH groups of PEG and GA:

$$PEG/GA + AgNO_3 \rightarrow PEG/GA/Ag^+NO_3^-.$$

When adding reducers into the system silver atoms are formed by following chemical conversion:

$$PEG/GA/Ag^+NO_3^- + NaBH_4 + H_2O \rightarrow PEG/GA/Ag^0 + H_2 + B_2H_6 + NaNO_3,$$

$$PEG/GA/Ag^+NO_3^- + HCOOH \rightarrow PEG/GA/Ag^0 + CO_2 + HNO_3.$$

In both cases depending on temperature and reaction time, the change in color of solution first to yellow, then to dark brown and black (Figure 1) shows the reduction of silver ions.

It is known that X-ray phase analysis is one of the main methods which determines crystal phase. X-ray phase analysis of PEG–GA–Ag^0 composite was studied and in Figure 2 X-ray phase spectra of reduction products performed at different temperatures are given.

As is seen from Figure 2, according to results of analysis of polymer composites obtained in PEG:GA=2:1 mass ratio at pH=11 and 293–353 K temperature range depending on temperature sizes of silver nanocomposites vary in the range of 7–9 nm.

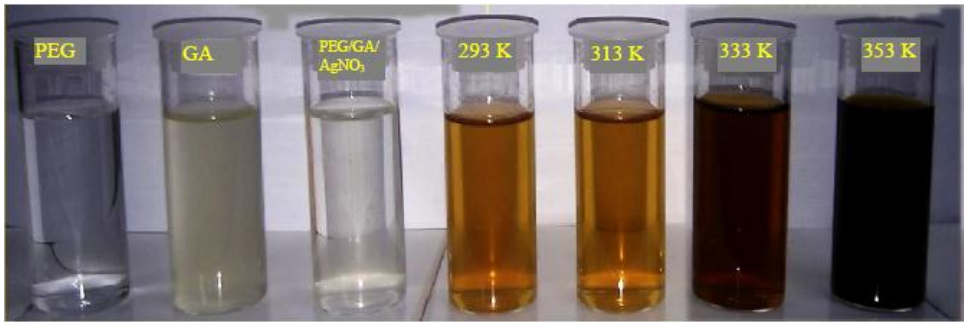

Fig. 1. Depending on reaction time the change of color of PEG–GA–Ag^0 suspension.

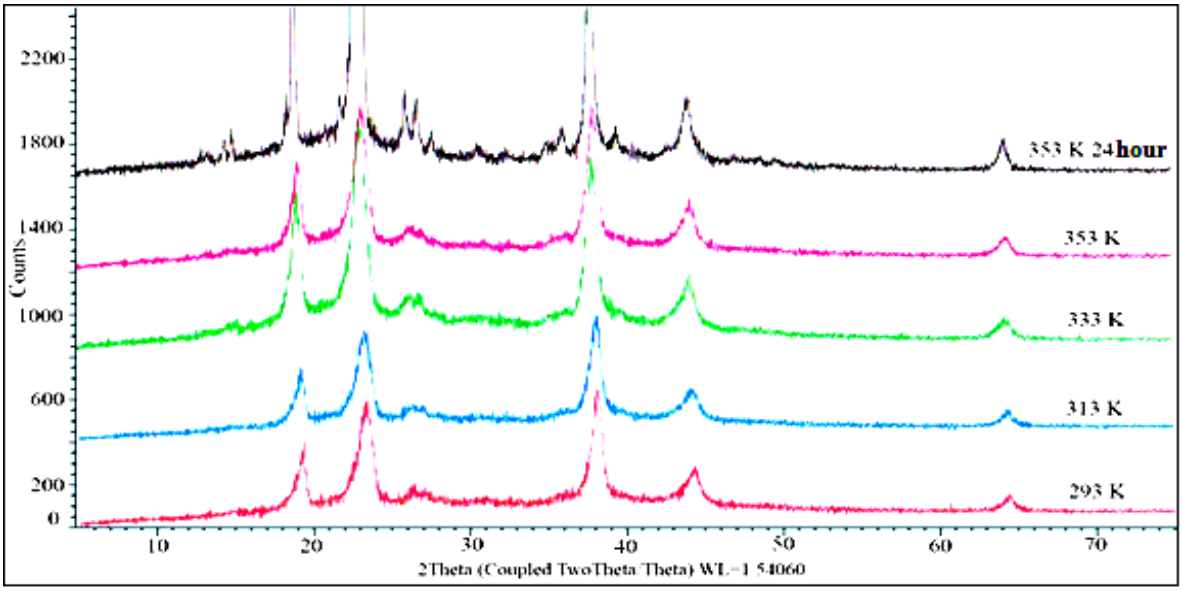

Fig. 2. X-ray spectra of PEG/GA/Ag^0 composite obtained at different temperatures. The spetra at 353 K given as 24 hours differs from previous examples by the maintenance of for 24 hours a day. In comparison with other examples it shows there are no aggregated Ag-NPs.

In spectrum, we observed 19.23^0 and 23.34^0 strong and 13.61^0, 27.32^0 weak reflections at angle 2θ typical for PEG and GA amorphous system. 37.91^0, 43.71^0, 64.06^0 and 76.98^0 degree values of Bragg reflection at angle 2θ for silver nanoparticles are determined by corresponding (111), (200), (220), (311) crystalline regions. This shows the formation of silver nanoparticles in centered cubic shape. High intensity of the peak corresponding to (111) field justifies the existence of nanoparticles. Average value of dimensions of Ag nanoparticles is calculated by Debye–Scherrer equation:

$$n = \frac{K\lambda}{\beta \cos\theta},$$

where K – Scherrer constant (0.9–1), λ – X-ray wavelength (1.5418 A), $\beta_{1/2}$ – width of X-ray peak and θ – Bragg angle. By Scherrer equation, it was determined that average sizes of particles are found to be 7–9 nm depending on the reaction time and temperature.

By parallel experiments, it was determined that the sizes of silver nanoparticles produced at high temperature from 292 to 353 K, increase when PEG/GA is not used. This confirms the stabilizing function of polymer macromolecules without any changes in nanosizes of Ag nanoparticles for a long period. At the high temperature of over 353 K nanosizes of particles increases. This can be explained by high flexibility of polymer macromolecules and aggregation process in silver atoms.

Cht is a biologically active natural polysaccharide β-1,4 connected with deacetylated D-glucosamine residues with N-acetyl-D-glucosamine residues. High bioconformity, degradation ability, non-toxical property, bioactivity, and multifunctionality caused study of it as a natural cation exchanger biopolymer. From this point many research works are dedicated to the use of chitosan with another synthetic polymer in biomedical purposes, pH sensitive medical preparations and in stabilization of metal nano particles.

Using $NaBH_4$ and HCOOH Ag^0 nanoparticles were synthesized with (Cht) and it was determined that Ag^+ ions form coordination around $–NH_2$ and –OH groups in Cht. In Cht, medium reduction of silver ions and formation of different color changes occurs similar to PEG:GA systems. It was determined that to stabilize experiments in relatively small sizes in chitosan medium of Ag^0 nanoparticles the process should be performed 1 hour in the range of 323–343 K.

In Figure 3 (*a*, *b*) obtaining spectra of silver nanoparticles in chitosan medium.

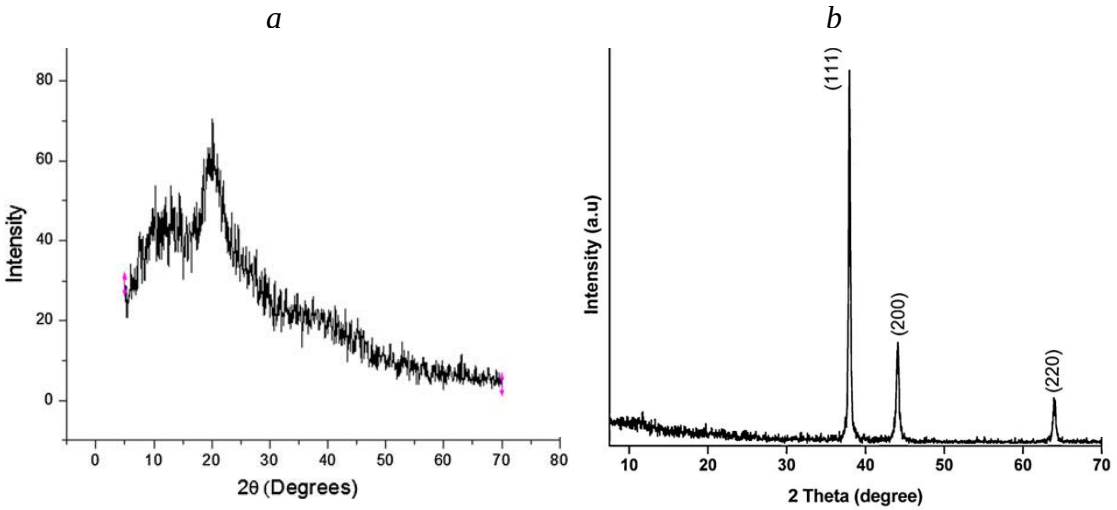

Fig. 3. *a* – X-ray spectrum of chitosan, *b* – X-ray spectrum of Chitosan–Ag^0 composite

As it is seen, peak typical for crystal phase is not observed in X-ray spectrum of (Cht). But in Cht.-Ag^0 spectrum in 2θ three strong intensiveness is formed typical for silver atoms. These are crystal phases which conform to 37.86^0, 43.68^0 and 64.12^0 values of Bragg reflection in 2θ for Ag^0 nanoparticles. It was determined that average sizes of nanoparticles are found to be 8–11 nm depending on reaction period and temperature.

Conclusion

We have synthesized colloidal Ag^0 nanoparticles with PEG/GA and Cht. Results of X-ray analysis show that Ag^0 nanoparticles are in centered cubic crystal shape and depending on temperature sizes of particles changes in the range of 7–9 and 8–11 nm corresponding to PEG/GA, Cht medium.

References

1. Abou K.M. El-Nour, Eftaiha A., Al-Warthan A., Ammar R.A. Synthesis and applications of silver nanoparticles // Arabian J. Chem. 2010. No 3. P. 135–40.
2. Cho K.H., Park J.E., Osaka T., Park S.G. The study of antimicrobial activity and preservative effects of nanosilver ingredient // Electrochim. Acta. 2005. No 51. P. 956–960.
3. Du B.D., Phu D.V., Duy N.N., Lan N.T. and Lang V.T. Preparation of colloidal silver nanoparticles in Poly(vinylpyrrolidone) by γ-ray irradiation // J. of Exp. Nanoscience. 2008. No 3. P. 207–213.
4. Wei D., Sun W., Qian W., Ye Y. and Ma X. The synthesis of chitosan based silver nanoparticles and their antibacterial activity // Carbohydrate Res. 2009. No 344. P. 2375–2382.
5. Gottschalk F., Nowack B. The release of engineered nanomaterials to the environment // J. Environ. Monit. 2011. No 13. P. 131145−1155.
6. Ahmad A., Mukherjee P., Senapati S. Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium oxysporum // Colloids Surf. B Biointerfaces. 2003. No 28. P. 313–18.
7. Bai J.L., Du Y.J. One-pot synthesis of polyacrylamide-gold nanocomposite // Mater. Chem Phys. 2007. No 106. P. 412–20.
8. Caro C., Castillo P.M., Klippstein R. Silver nanoparticles: sensing and imaging applications. In: Perez DP, ed. Silver nanoparticles // Rijeka, Croatia: InTech. 2010. P. 201–224.
9. Guo J.Z., Cui H., Zhou W., Wang W. Ag nanoparticle-catalyzed chemiluminescent reaction between luminol and hydrogen peroxide // J. Photochem. Photobiol. A: Chem. 2008. No 193. P. 89–96.
10. Lengke M.F., Fleet M.E., Southam G. Biosynthesis of silver nanoparticles by filamentous cyanobacteria from a silver (I) nitrate complex // Langmuir. 2007. No 23. P. 2694–2699.
11. Rai M., Yadav A., Qade A. Silver nanoparticles as a new generation of antimicrobials // Biotechnol. Adv. 2009. No 27. P. 76–83.
12. Thakkar K.N., Mhatre S.S., Parikh R.Y. Biological synthesis of metallic nanoparticles // Nanomedicine Nanotechnol. Biol. Med. 2010. No 6. P. 257–62.
13. Valizadeh A., Mikaeili H., Samiei M. Quantum dots: synthesis, bioapplications, and toxicity // Nanoscale Res. Lett. 2012. No 7. P. 480–93.

14. Zhu S., Du C., Fu Y. Fabrication and characterization of rhombic silver nanoparticles for biosensing // Optical Mater. 2009. No 31. P. 769–74.
15. Hussain J.I., Kumar S., Hashmi A.A., Khan Z. Silver nanoparticles: preparation, characterization, and kinetics // Adv. Mat. Lett. 2011. No 2. P. 188–194.
16. Banerjee P., Satapathy M., Mukhopahayay A. and Das P. Leaf extract mediated green synthesis of silver nanoparticles from widely available Indian plants: synthesis, characterization, antimicrobial property and toxicity analysis // Bioresour. Bioproces. 2014. No 1. P. 3–12.
17. Sadeghi B., Jamali M., Kia Sh., Amininia A., Ghafari S. Synthesis and characterization of silver nanoparticles for antibacterial activity // Int. J. Nano Dim. 2010. No 1. P. 119–124.
18. Pan W., Chen Y. Preparation of Ag–Polyacrylamide Nanocomposites by Ultraviolet Irradiation Technique // Appl. Mechanics and Mater. 2010. No 44–47. P. 2199–2202.
19. Melissa Kemp M., Kumar A., Mousa S., Tae-Joon Park, Ajayan P., Kubotera N., Mousa S.A. and Linhardt R.J. Synthesis of Gold and Silver Nanoparticles Stabilized with Glycosaminoglycans Having Distinctive Biological Activities // Biomacromol. 2009. No 10. P. 589–595.
20. Ahmad M.B., Tay M.Y., Mohd K.S., Hussein Z. and Lim J.J. Green Synthesis and Characterization of Silver/Chitosan/Polyethylene Glycol Nanocomposites without any Reducing Agent // Int. J. Mol. Sci. 2011. No 12. P. 4872–4884.
21. Govindan S., Nivethaa A., Saravanan R., Narayanan V., Stephen A. Synthesis and characterization of chitosan–silver nanocomposite // Appl. Nanosci. 2012. V. 2. P. 299–303.
22. Dmitruk N.L., Borkovskaya O.Y., Mamontova I.B., Mamykin S.V., Malynych S.Z. and Romanyuk V.R. Metal nanoparticle-enhanced-photocurrent in QAAs photovoltaic structures with microtextured interfaces // Nanoscale Res. Lett. 2015. No 10. P. 72–76.
23. Pencheva D., Bryaskova R., Kantardjiev T. Polyvinyl alcohol/silver nanoparticles (PVA/AgNps) as a model for testing the biological activity of hybrid materials with included silver nanoparticles // Mater. Sci. and Eng. 2012. V. 32. P. 2048–2051.
24. Ushakov N., Radchuk N., Ushakov A. Optical properties of metallic nanoparticles trapped by arabinoqalactan molecule. Photonics, Devices, and Systems, VI // Mater. Conference Praque Gzech Republic. 2015. V. 9450. P. 87–92. 2014, 27 August.

MÜXTƏLİF POLİMERLƏR MÜHİTİNDƏ GÜMÜŞ NANOHİSSƏCİKLƏRİNİN SİNTEZİ

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Orta molekul kütləsi 200 kDa olan qummiarabik və 40000 olan polietilenqlikol eləcədə 200 kDa olan xitozan mühitində kiçik qatılıqlı $NaBH_4$ və HCOOH məhlulları iştirakı ilə 293–353 K temperatur intervalında, müxtəlif reaksiya müddətində Ag^0 nanohissəciklərinin alınması və stabilləşdirilməsi həyata keçirilmişdir. Alınmış gümüş nanohissəciklərin ölçüləri rentgen-faza analizi ilə tədqiq edilmişdir. Müəyyən olunmuşdur ki, stabilləşdirici kimi polietilenqlikol və qummiarabik əsaslı birgə polimerlər mühitində formalaşan gümüş nanohissəciklərinin ölçüləri 7–9 nm, təbii poliaminosaxarid olan xitozandan istifadə etdikdə stabilləşən gümüş nanohissəciklərinin ölçüləri isə 8–11 nm aralığında dəyişir.

Açar sözlər: *gümüş nanohissəciklər, qummiarabik, xitozan, polietilenqlikol, nanokompozitlər, Rentgen-faza analizi.*

СИНТЕЗ НАНОЧАСТИЦ СЕРЕБРА В РАЗЛИЧНЫХ ПОЛИМЕРНЫХ СРЕДАХ

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В среде гуммиарабика со средней молекулярной массой 200 кДа, полиэтиленгликоля 40000 и хитозана 200 кДа, с участием растворов низких концентраций $NaBH_4$ и HCOOH в температурном интервале 293–353 К и различных временах реакции осуществлены получение и стабилизация наночастиц серебра. Размеры полученных наночастиц серебра исследованы рентгенофазовым анализом. Установлено, что с использованием в качестве стабилизатора сополимера на основе полиэтиленгликоля и гуммиарабика размеры с формированных наночастиц серебра составили 7–9 нм, а в среде природного полиаминосахарида, такого как хитозан, размеры стабилизованных наночастиц серебра меняются в пределах 8–11 нм.

Ключевые слова: *наночастицы серебра, гуммиарабик, хитозан, полиэтиленгликоль, нанокомпозиты, Рентген-фазовый анализ.*