# CHITOSAN POLYMER COMPOSITE MATERIAL CONTAINING OF SILVER NANOPARTICLE

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We obtained $Ag^0$ nanoparticlesusing $NaBH_4$ as a reducer by chitosan with 200 kDa average molecular mass at various reaction times. $Ag^0$ nanoparticles were studied by X-ray diffraction analysis, UV-vis, FTIR-spectroscopy and SEM. It was shown that when using natural polyaminosaccharide chitosan as a stabilizer, sizes of silver nanoparticles make 14-25 nm depending on reaction period. We determined by FTIR-spectroscopy that $–NH_2$ (mainly) and –OH groups in chitosan macromolecule participate in stabilization of $Ag^0$ nanoparticles. According to UV-visspectroscopy the $Ag^0$ nanoparticles shows surface plasm resonance in 410 nm.

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*Keywords*: *silver, nanoparticle, stabilization, chitosan, X-ray, SEM.*

## 1. Introduction

Recently the investigation of Cu, Au, Ag, Pt and Pd nanoparticles containing polymer composites has been the main research objects of scientific communities. Optical, catalytic, medical materials prepared on the basis of these composites differ from their precursors for higher qualities [1,2]. The size of metal nanoparticles determinetthat their direct application field. The sizes of metal nanoparticles can be controlled depending on nature of selected stabilizing and reducing agent and the condition of the process [3,4].

It is kown that silver nanoparticles are widely used in preparation of stabilized composites, biosensors, antibacterial preparations in medicine and drug delivery [5,6]. The use of some biopolymers as a stabilizing agent leads to wide spectrum impact possibilities of obtained nanocomposite. Chitosan is a natural polysaccharide which is generated from β-1,4 compound of glucosamine (Fig.1) and N-acetyl glucosamine chain [7].

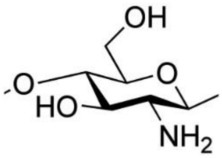

*Fig. 1. Chitosan macromolecule*

Chitosan is an antimicrob, antibacterial natural large molecular compound which does not form toxic compounds in human organism when decompose by the impact of ferments. High therapy possibilities and antimicrob properties of silver nanoparticles were studied many times by researchers. Many scientific works on the use of Ag nanoparticles in treatment of cancer can be found in literature data [8,9]. But the disadvantage is that when using >20 nm Ag nanoparticles in free state we observed toxic effects on healthy cells.

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Synthesized $Ag^0$ nanoparticles with chitosan without using any reducing reagent. Reduction was conducted under 15 psi pressure and at 393K. Catalytic property of chitosan-$Ag^0$ composite was tested in reduction reaction 4-nitrophenol. Antimicrob activity of nanocomposite was tested on *Escherichia coli* and *Micrococcus luteus*and its inhibitor property was determined [10]. Analysis of literature data shows that by using starch, agar-agar, cellulose, gum arabic, arabinogalactan, chitin and other natural polysaccharides obtaining of Ag nanocomposites is now one of the promising directions [11,12]. In our paper we studied obtaining and structure of $Ag^0$ nanoparticles by using $NaBH_4$ as a reducer and chitosan both as a reducer and stabilizing agent.

## 2. Experimental

### Materials

The stabilizing agent chitosan is 97% chemcially pure (deacetylation degree is 84%), its average molecular mass is 200 kDa and was purchased from Sigma Aldrich. $AgNO_3$ was used as a silver precursor (99.98%) and is manufactured by Merck company (Germany). All other chemical reagents - sodium borohydride (98% $NaBH_4$), acetic acid ($CH_3COOH$), deionized water and percipitates are chemically pure and from Fluka.

### Synthesis of Ag collodial

0.5 gr chitosan is dissolved in 25 ml 1% acetic acid solution and mixed 15 minutes. The solution is filtered and 5 mL $2.5\times10^{-2}$ M $AgNO_3$ is added into it and mixed 2 hours at room temperature. Then 10 ml $NaBH_4$ with concentration of 0.04 M is added into the solution. Instantly color of the solution changes from yellow to dark brown. After mixing the suspension at 293K 1 hour, it is precipitated, washed out under atmospheric pressure first with ethanol, then with bidistilled water 2-3 times and dried and brought to a stable mass. To study the molar ratio of reagents, temperature, reaction time on obtained silver nanoparticles the process was investigated at 293, 313, 333, 353 K temperatures, m(chitosan):m($AgNO_3$) different mass ratios and 5, 10, 20, 30 and 60 minutes intervals.

### Instrumentation and measurements

UV-Vis spectral measurements were recorded on Shimadzu UV-visible spectrometry (UV-1650PC-Tokyo, Japan) at from 300 nm to 700 nm interval. Chemical shift of functional groups was confirmed on IR-spectroscopy (FTIR) with Fourier transformation at 300-4000 $sm^{-1}$ regions (Shimadzu). X-Ray diffraction pattern were recorded with Advance-D8 (Bruker), X-ray diffractometer with Cu $K\alpha=1.054$ A.U, radiation for $2\theta$ values of over 200- 700. Surface morphology of nanocomposite was studied on Scanning Electron Microscope (SEM S4700, Hitachi).

## 3. Result and Discussion

High biocompatibility, biodegradation, non-toxicity, bioactivity and multifunctionality of chitosan have been a reason for studying it as a natural cationite biopolymer many years. From this point many research works can be found in literature data on using chitosan for biomedical purposes, using it with other synthetic polymer for stabilization of pH sensitive drug carriers. As it was stated our main aim is to study the synthesis and structure of $Ag^0$ ions by $NaBH_4$ as a reducer with chitosan. $Ag^+$ ions form coordination around $-NH_2$ and $-OH$ groups in chitosan.

$$\text{Cht.} + AgNO_3 \rightarrow \text{Cht.}/Ag^+\ NO_3^-$$

When adding $NaBH_4$ into the system reduction of silver ions goes according to the following chemical equation:

$$\text{Cht.}/Ag^+\ NO_3^- + BH_4^- + 3H_2O \rightarrow \text{Cht.}/Ag^0 + 3.5H_2 + B(OH)_3$$

*Fig. 2. Color variations depending reduction time of chitosan-Ag$^0$ suspension*

As it is seen from figure 2 during reduction process color of the solution changes first to yellow, then to dark brown. This shows the formation of Ag$^0$ nanoparticle containing colloidal solution.

One of the physical-research methods which shows formation of Ag$^0$ nanoparticles is UV-spetroscopy. We recorded UV spectra of the samples when nanoparticles are formed in reduction process. All spectrashows a strong peak associated with surface plasmon resonanse centered in 410. This data is agreed to literature, a previous study reported the plasmon resonanse peak near 400 nm with Ag nanoparticles of 12±2 nm. If a maxmimum peak betwenn 405-418 nm with Ag nanoparticles size of 9-30 nm[13].

As it is seen from figure 3 when reduction time increases intensity of peak rises and absorption band forms maximum adsorption due to full conversion of Ag$^+$ ions to Ag$^0$ atoms within 1 hour. When the reduction process proceeds more than 1 hour, intensity of peak does not change. 350-450 nm interval of plasm resonance of Ag$^0$ nanoparticles shows that sizes of silver nanoparticles in suspension are distributed in narrow fraction. During reduction process at 353-363 K temperature with the increase of temperature of samples formation of Ag$^0$ nanoparticles accelerates. Variation is observed on spectra due to flexibility of chitosan macromolecule and increasing the energy of system at 363K.

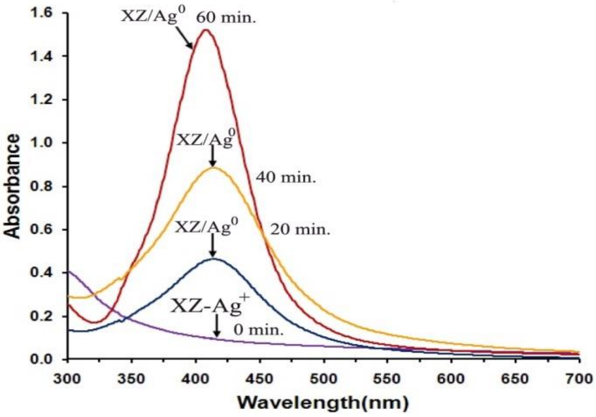

*Fig. 3. UV visible spectrum of formation of Ag$^0$ nanoparticles depending on time with the use of chitosan*

Thus, adsorption of 405 nm intensive peak of Ag$^0$ nanoparticles reduces and the curve becomes to widen. According to the researches to stabilize Ag$^0$ nanoparticles in small size at chitosan medium the process must be performed 1 hour at 323-343 K. It is known that X-ray phase analysis is one of the methods which determines crystal phase. X-ray phase spectrum of stabilized Ag$^0$ nanoparticle containing polymer composite was recorded (Fig. 4).

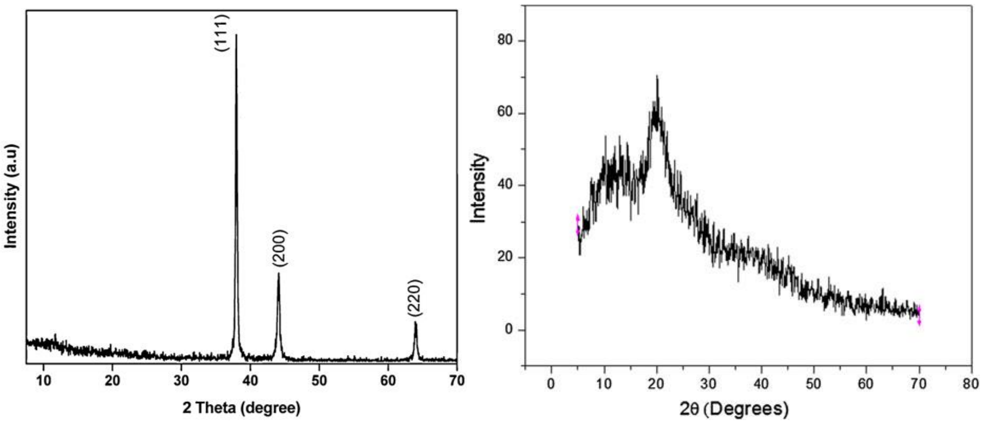

*Fig. 4. X-ray phase spectrum of chitosan (left) and chitosan-$Ag^0$composite (right).*

As it is seen the peak of crystal phase in X-ray phase spectrum of chitosan is not observed. But in 2θ three strong intensities, which belong to silver atoms, are formed in chitosan-$Ag^0$ spectrum. These are crystal phases with (111), (200) and (220) areas which conform to $37.86^0$, $43.68^0$ and $64.12^0$ values of Bragg reflection in 2θ for Ag nanoparticles [14,15]. Obtained X-ray phase results show that Ag nanoparticles exist in centered cubic form in chitosan. The sizes of Ag nanoparticles stabilized in polysaccharide were determined by Debye-Scherrer equation:

$$n=K\lambda/\beta cos\theta$$

where K – Scherrer constant (0.9÷1), λ – X-ray wavelength (1.5418 A), $\beta_{1/2}$width of X-ray peak and $\theta$ Bragg angle. It was determined that average sizes of nanoparticles make 14÷25 nm depending on reaction time and temperature. SEM study of synthesized chitosan-$Ag^0$composite was performed. Chitosan-$Ag^0$ nanocomposite nanoparticles are stabilized in more oval granules.
The scanning electron microscopy (SEM) image of chitosan-silver is presented in Figure 5. The image reveals the surface structure of chitosan-silver nanocomposite.

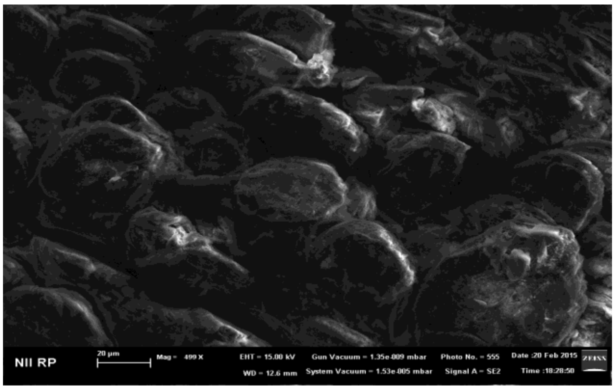

*Fig. 5. SEM images of chitosan-silver nanocomposite*

It shows that Ag are nano-spherical with size 12 and 23 nm. Since chitosan molecules acts as a reducing agents in presence of aqueous sodium borohydride, even after drying the chitosan molecules does not allow silver nanoparticles to get merge with each other. Thus in SEM image these particles appear as nano sized ones.

Probably, chitosan macromolecules or its $-NH_2$ and -OH functional groups enclose Ag nanoparticles together with polymer chain. Interaction between $Ag^0$ nanoparticles and chitosan macromolecule was confirmed by FT-IR-spectroscopy (Fig.6).

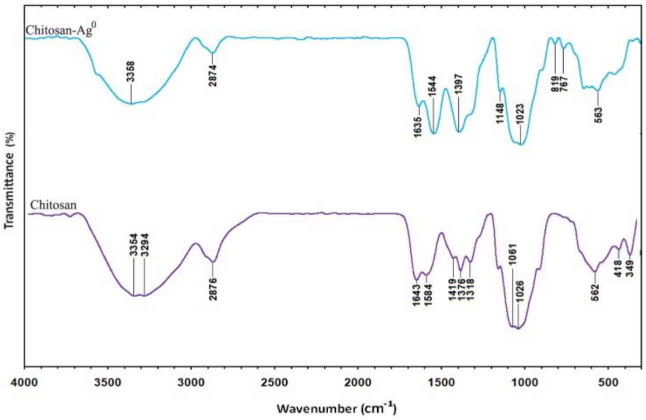

*Fig.6. Structural unit of chitosan macromolecule and FTIR spectra of chitosan-Ag$^0$ composite*

We observed bands in 3354 and 3294 sm$^{-1}$ region typical for O-H and N-H vibration bonds in FT-IR spectrum of chitosan. 2876 sm$^{-1}$ adsorption band shows distorted chemical shift of aliphatic C-H bond, 1643 and 1584 sm$^{-1}$ show N-H chemical bond, 1419, 1376 and1318 sm$^{-1}$intensities show aliphatic C-H chemicalbond, 1061 and 1026 sm$^{-1}$ adsorption bands are the peaks which conform to C-O bond [16-18]. As it is seen in chitosan-Ag$^0$ spectrum marked with blue line, 1643 and 1584 cm$^{−1}$ adsorption bands are exposed to chemical shift up to 1635 and 1544 cm$^{−1}$ correspondingly. In 1544 sm$^{-1}$ high intensive peak is observed. In 1397 sm$^{-1}$ distorted bond of chitosan-Ag$^0$ complex characterizes the interaction between Ag nanoparticles and chitosan. Thus, when amine and hydroxyl groups in chitosan enclose Ag$^0$ nanoparticles spheric stabilized (XZ-Ag$^0$)$_n$ system is formed. The interaction or stable state of the system occurs due to electrostatic interaction forces between negatively charged functional groups in basic chitosan and partially positively charged metal nanoparticles and van der waals forces [19-21]. According to this we may show schematic formula (Fig.6) of stabilization of Ag nanoparticles with chitosan macromolecules.

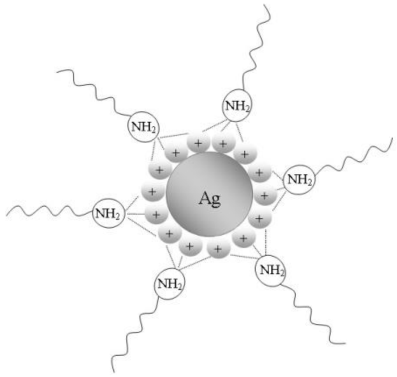

*Fig.6. The suggestet structural form of silver nanoparticles which stabilizing by chitosan.*

## 4. Conclusion

Chitosan–silver nanocomposite was synthesized using simple chemical method. The XRD patterns of chitosan and chitosan-silver are seen to be free from impurity peaks and the respective XRD patterns indicate the formation of chitosan-silver nanocomposite clearly. The SEM image of Ag indicates the formation of spherical nanoparticles which are of uniform size. The chitosan–silver nanocomposite the silver nanoparticles are seen to be enveloped by chitosan, and agglomeration is also observed. It is evident that agglomeration can be prevented on dispersing Ag in chitosan for a longer duration of time. The shift in the peaks of chitosan observed in the FTIR spectrum indicates the formation of chitosan–silver composite. All the characterizations done that the chitosan–silver nanocomposites have been prepared successfully.

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