Bimetallic Chitosan-stabilized Nanoparticles Ag/Cu, Ag/Co with Fungicidal Properties

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Research Article

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Abstract

Synthesized chitosan stabilized bimetallic nanoparticles Ag/Cu and Ag/Co. It was found that the size and shape of bimetallic nanoparticles can be controlled by varying the concentration of the reducing agent – NaBH_4 and the molar ratios of metal ions.

Established that an increase in the concentration of the reducing agent, as well as metal ions, promote the formation of fibrillar nanoparticles. It was found that solutions of the synthesized samples effectively suppress the growth and development of the phytopathogen - *Fusarium oxysporium* forming a sterile zone from 13.3 to 36 mm.

Introduction

It is obvious that the development of nanochemistry is progressing at a rapid pace. Among the directions that have emerged in the last 2-3 years, one can note: reduction of particle size to 1-3 nm and synthesis of sub nanoparticles less than 1 nm; obtaining not only spherical particles, but also particles of other shapes: cubic, rings, tubes, nesting dolls, needles; expansion of work on structures of the "core-shell" type; control of the process of self-organization of nanoparticles by changing the temperature and pH of the medium and obtaining hybrid particles, including inorganic and organic compounds [1–6].

Among them, the synthesis of bimetallic NPs of the "core-shell" type is of particular fundamental applied interest, since this method makes it possible to obtain nanomaterials with improved and complex properties. Despite the high adsorption capacity of chitosan, the effective catalytic activity of its bimetallic complex has been noted in several literature sources. In particular, the complex of chitosan with bimetals $\text{Cu(II)-Fe(III)/H}_2\text{O}_2$ turned out to be more effective in removing dyes [7]. The above structural study suggests that the addition of Cu (II) did not significantly affect the interaction between Fe (III) and the chitosan polymer. In CS-Cu-Fe-1 bimetal complex, Fe (III) was still hexacoordinated to chitosan molecules, complexing through equal O and N atoms of the chitosan polymer and water molecule while Cu (II) was tetra coordinated to chitosan molecules and chelated with more O atoms than N atoms of the chitosan polymer.

In the present study, various bimetallic nanoparticles Ag-Au, Ag-Pd, Au-Pd were synthesized using natural biopolymer gum kondagogu as a reducing and sealing agent in a simple and economical method [8–12]. The average particle size of Ag-Au, Ag-Pd, and Au-Pd BNPs was found to be 23 ± 10.3 , 21 ± 7.6 and 23 ± 9.4 nm respectively. The bimetallic nanocomposites were evaluated for their catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol in the presence of NaBH_4 . The catalytic efficiencies of three bimetallic nanocomposites were of the following order Ag-Pd > Ag-Au > Au-Pd. This study establishes the catalytic potentials of the three different bimetallic nanocomposites in the reduction of 4-NP an environmental pollutant, and the impact of their synergistic property [8].

It was also found that the bimetallic complex chitosan-Fe/Al is more effective for water purification from nitrates (NO_2^- , NO_3^- , NH_4^-) at low temperatures than at usual [13–15]. pH is a key factor affecting the efficiency of nitrate purification. The rates of adsorption and reaction were higher under acidic conditions than under alkaline conditions.

It was found that nanoparticles of the Cu/Mg-chitosan bimetallic complex are two times more effective than chitosan in wastewater purification from dyes. The adsorption of the dye is 99% in the Cu/Mg-chitosan complex compared to 49% in chitosan [16–17].

A magnetic polyelectrolyte complex (PEC) based on chitosan and sodium ligninsulfonate as a carrier for stabilizing bimetallic Fe/Pd particles (m-PEC-Fe/Pd) was synthesized to decompose and decolorize organic pollutants in an aqueous solution [18–19]. Due to its high removal efficiency, reaction rate, easy separation and good recyclability, m-PEC-Fe/Pd has the potential to become an environmental recovery material for the treatment of wastewater containing organic compounds.

The morphology of bimetallic complexes in the presence of polymers depends on various factors. For example, it was shown that the morphology of "foamy" complexes with chitosan and polystyrene block (4-vinylpyridine)] PSP-4-PVP in the presence of Au/Ag depends on both the nature of the polymer and the molar ratio of the polymer / metal salt [20–22]. Polymer PSP-4-PVP in a 1:1 ratio form the most porous morphologies.

Pd/Co NP were deposited on chitosan for the production of a new heterogeneous recyclable catalyst for use in the reaction of bimetallic catalytic reduction [23]. Nanocomposites-catalysts used in the reduction of nitro aromatic compounds using NaBH_4 at room temperature. Various aromatic amines and diamines were used in the reduction reaction. Aromatic amines were obtained as the only product of the reduction reaction with 15 mol% Pd and 12 mol% Co for 2 hours. This reaction had several advantages such as mild reaction conditions, high yield, and green solvent and recyclable catalyst.

Metal-polymer nanostructured composites are promising materials, since they open up the possibilities of combining absolutely different organo-inorganic compounds with different properties in one material due to synergy. In this regard, the production of hybrid nanomaterials with improved operational properties containing mono- and / or bimetallic nanoparticles is an urgent task.

Obviously, this is due to the unique properties of nanoparticles (NPs), which are successfully used in engineering, technology, biomedicine, etc. In this regard, the antitumor activity of magnetic Ag-Fe nanoparticles with «a Janus-nanoparticle» structure obtained by the method of electric explosion of a conductor was studied. The combined electrical explosion of silver and iron wires in an argon atmosphere produced spherical particles 72 nm.

Found that Ag and Fe are unevenly distributed over the particles. There are areas enriched in one of the components, with clear boundaries of phase separation, or "Janus" of nanoparticles. In the diffraction pattern of the sample, the main reflections correspond to the phases of metallic Ag and Fe. As a result of

the electric explosion of wires made of immiscible metals iron and silver, bimetallic Ag-Fe nanoparticles with a Janus structure were obtained. Ag-Fe nanoparticles demonstrate a higher antitumor activity than individual metals. Such particles can be promising for the creation of drugs for magnetic delivery purposes [24]. The authors obtained composites based on bimetallic NPs Ag–Cu stabilized with polyvinyl acetate (PVA) with bioactive properties [25].

Thus, the development of methods for obtaining bimetallic NPs and the strategy of their stabilization, as well as the identification of possible directions of their application, is of fundamental applied interest.

Materials And Methods

For obtaining of bimetallic complex have been used CS *Bombyx mori* with molecular mass 200000 and degree of deacylation 70%. Were used metal salts such as NaBH_4 , CoCl_2 , CuSO_4 and AgNO_3 grade “chemically pure”.

Obtained samples were investigated by the elemental analysis. Emission qualitative spectral analysis (MP003:15, 5 accuracy category). Qualitative spectral analysis is based on the individuality of the optical line spectrum of the radiation of atoms of each element of the periodic table, which is determined by the structural features of their electronic shells. The appearance of optical line spectra of atoms of elements is due to the excitation and emission of valence electrons located on the outer shells of atoms. The excitation energy of such electrons is from 15 eV.

Morphology of nanostructured film systems were investigated on an electronic microscope SEM EVO MA 10 (Carl Zeiss, Germany), atomic-force microscope AFM Agilent 5500 (USA) at room temperature. Silicon cantilevers with rigidity 9.5 N/m with frequency 145 kHz were used. Maximum field of scanning at AFM by X, Y was $15 \times 15 \mu\text{m}^2$, by Z – 1 μm .

Method of static and dynamic light scattering (photon correlation spectroscopy) DLS. The range of measured sizes is in the range from fractions of nm to 5-10 microns. The analyzer's laser power ranges from 2 to 35 mW. All Photocor analyzers have a mode for automatic measurements, processing and presentation of analysis results.

Experimental Part

Synthesis of chitosan-stabilized bimetallic nanoparticles Ag/Cu, Cu/Co

Chitosan-stabilized bimetallic nanoparticles (BNPs) were obtained in the presence of NaBH_4 according to the procedure [26]. NPs are formed accordingly the following mechanism:

Table 1

Determination of the mass fraction of metals by spectral analysis. pH=6, t=22°C, recovery NaBH₄, stabilizer - CS. Mw(CS)-200000, DD(CS)-70%

№	BNPs samples	Theor. (Me ²⁺ /Ag ⁺), %	Ag, %		Cu ²⁺ , %		Co ²⁺ , %	
			ions	NP	ions	NP	ions	NP
1	Cu ²⁺ /Ag ⁺ =2:1	5.74/5.6	0.6	5.0	0.04	5.70	-	-
2	Cu ²⁺ /Ag ⁺ =2:1	5.78/5.78	0.08	5.7	0.02	5.76	-	-
3	Cu ²⁺ /Ag ⁺ =2:3	5.78/5.64	0.04	5.6	0.06	5.72	-	-
4	Co ²⁺ /Ag ⁺ =1:1	5.74/5.6	-	-	0.06	5.68	0.05	5.54

As the results depicted that under the selected conditions for the preparation of BNPs, only traces of metal ions were found in the final product, i.e. 98% of metal ions are reduced and converted into NPs.

Controlling the size, shape, and structure of metallic NPs is technologically important because of the strong correlations between these parameters and biologically active properties. The size and shape of metal NPs were controlled by varying the concentration of the reducing agent (Table 2).

Table 2

Influence of synthesis conditions on the size and shape of chitosan stabilized BNPs, Mw (CS)-200000, DD(CS) -70%, reducing agent- Na₃B₄O₇

№	n (NaBH ₄), 10 ⁻⁴ mol	The ratio of the reaction mixture, mole	Size of NPs, nm (by AFM)	Shape of NPs (By AFM)
1	1.3	Cu ²⁺ /Ag ⁺ =2:1	50÷500	Spherical
2	2.0	Cu ²⁺ /Ag ⁺ =2:1	75÷400	Spherical
3	2.0	Cu ²⁺ /Ag ⁺ =2:3	d=180÷260 h=25 micron	needle-like
4	2.6	Ag ⁺ /Co ²⁺ =1:1	400÷650	spherical, non-spherical

It should be noted that the size and shape of the forming Cu/Ag nanoparticles depends on the concentration of the reducing agent and the concentration of metal ions, i.e. an increase in the

concentration of the reducing agent leads to a regular narrowing of the particle size (examples 1 and 2), and an increase in the concentration of metal ions contributes to the formation of needle-shaped nanoparticles (example 3), $d=180-260$ nm and $h=25$ micron. When in the ratio $Ag^+/Co^{2+}=1:1$, were formed spherical and nonspherical NPs in the size range of 400-650 nm.

DLS-studies of chitosan solutions stabilized BNPs - Cu/Ag and Co/Ag

The dimensional characteristics of chitosan-Cu/Ag and chitosan-Co/Ag in solution have been investigated. The results demonstrate that NPs were formed in the system, mainly from 25 to 200 nm. For example, for sample #1 this is 76%, and for sample #3 is 73%.

Note that 4.4% of NPs (sample #1) were up to 6 nm in size, only 12% of NPs were agglomerated. It is gratifying that a large number of particles had a size in the range of 130-500 nm, namely, 75.5% Cu/Ag BNPs had a size of - 137 nm and a size of 7.7% BNPs was 400 nm.

DLS measurements illustrate that in the solution of sample #2, containing 12% Cu/Ag BNPs, the particles have a size in the range of 2-32 nm, and 14.5% bimetallic particles are aggregated. Although of 73% of the BNPs was the size about 160 nm.

According to the results of DLS-studies, it can be seen that in the solution of sample #3 containing 11% Cu/Ag BNPs have a size of 184 nm, and 21% bimetallic particles are aggregated to large micron particles. Despite this, the size of 60% BNPs was about 160 nm.

As illustrated by the data of DLS-measurements of the size of sample #4, containing Ag/Co nanoparticles, the size of 6.5% of the particles was about 70 nm, and 42% of the bimetallic particles were aggregated to large micron particles. However, the size of 42.2% BNPs was about 700 nm. It is easy to see that relatively large BNPs were formed in this sample as compared to Cu/Ag BNPs. Perhaps this is due to the catalytic activity of cobalt ions, which could actively initiate the formation and growth of NPs.

Investigation of BNPs samples using an atomic force microscope (AFM)

The AFM images clearly demonstrated that Cu/Ag and Co/Ag nanoparticles of various shapes and sizes, which are practically evenly distributed (Fig. 1, a-d).

AFM image of the sample in fig. 4a containing Cu/Ag BNPs depicted that under the selected synthesis conditions were formed spherical BNPs from 50 to 450 nm. Additionally, the asymmetry of the histogram shows that BNPs differ in shape and size, which are distributed in the range from 5 to 750 nm. 14% NPs make up 250 nm. The roughness of the surface indicated that the distribution of BNPs over the polymer

matrix has a polymodal character. AFM image in fig. 4b containing Cu/Ag BNPs shows that under the selected synthesis conditions were formed non-spherical BNPs from 50 to 400 nm. It should be noted that defects of various shapes also appear on the surface of the films. The histogram is asymmetric the distribution range is narrow and ranges from 160 to 250 nm. The roughness of the surface indicates that the distribution of BNPs over the polymer matrix has a polymodal character, and the increased intensity is probably associated with the depth of the defect. AFM image of the sample in fig. 4c containing Cu/Ag BNPs illustrated that an increase in the concentration of the reducing agent during the synthesis of BNPs leads to the formation of fibrillar BNPs of various widths and lengths. It can be seen that BNPs grew in different directions with a diameter from 50 to 250 nm and a length of 25 μ m. It should be noted that the agglomeration of NPs in which they grow in one direction is also clearly visible on the surface of the films. The distribution histogram is asymmetric; the distribution range is narrow and ranges from 180 to 300 nm. The roughness of the surface indicated that the distribution of BNPs over the polymer matrix has a polymodal character, and the intensity ranges from 20 to 140 nm. It can be concluded that an increase in the concentration of metal ions contributes to the formation of fibrillar nanoparticles.

AFM image of the sample in fig. 4d demonstrated containing Co/Ag that under the selected synthesis conditions were formed spherical BNPs from 5 to 750 nm. The asymmetry of the histogram evidenced that BNPs vary in shape and size, which are distributed in the range from 5 to 500 nm, 30% of NPs are 500 nm in size. The roughness of the surface indicates that the distribution of BNPs over the polymer matrix has a polymodal character, with the intensity ranging from 20 to 160 nm.

Biologically active properties of BNP Cu/Ag and Co/Ag

The antagonistic activity of solutions containing BNPs was studied against of the phytopathogenic microorganism - *Fusarium oxysporium*. The researches were carried out in an artificial nutrient medium of according to the Chapek-Dox method [27].

Table 3

Fungicidal activity solutions of chitosan stabilized Cu/Ag and Co/Ag against *Fusarium oxysporium*

№	Samples	Sterile area, (mm)			
		I	II	III	Δd , mm
1	Registered drug <i>Bahor</i> (reference)	6	12	14	10.6
2	<i>Cu/Ag</i>	36	38	34	36.0
3	<i>Co/Ag</i>	14	12	14	13.3

As demonstrated the table 4, solutions of chitosan stabilized Cu/Ag and Co/Ag effectively prevented the growth and development of pathogens *Fusarium oxysporium* more than the registered standard - the drug *Bahor*. Perhaps this is due to the synergistic effects of the chitosan macromolecule and BNPs biogenic metals. These initial results are encouraging, and experimentation in this direction should be continued.

Conclusion

Thus, we have identified the conditions for obtaining bimetallic NPs - Cu/Ag and Co/Ag. It was found that by varying the concentration of the reducing agent and metal ions it is possible to regulate the size, shape, and type of the core and/or shell in chitosan stabilized BNPs. Preliminary studies of the bioactive properties of solutions containing Cu/Ag and Co/Ag show that BNPs effectively inhibit the growth and development of phytopathogens such as *Fusarium oxysporium*, forming a sterile zone from 13.3 to 36 mm.

Declarations

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Sample

Due to technical limitations, Sample #1, #2, #3 and #4 are only available as a download in the Supplemental Files section.

Figures

Figure 1

AFM images, distribution histogram and surface roughness of films of BNPs samples containing Cu/Ag and Co/Ag. a) Cu²⁺/Ag⁺=2:1, [NaBH₄]-1.3×10⁻⁴ mol; b) Cu²⁺/Ag⁺=2:1, [NaBH₄]-2.0×10⁻⁴ mol; c) Cu²⁺/Ag⁺=2:3, [NaBH₄]-2.0×10⁻⁴ mol; d) Co²⁺/Ag⁺=1:1, [NaBH₄]-2.6×10⁻⁴ mol

Supplementary Files

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- [Sample1To4.png](#)