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ARTICLE

Determination of Hydrodynamic Parameters of Chitosan Stabilized Bimetallic Nanoparticles

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ABSTRACT

The hydrodynamic characteristics of bimetallic Ag/Cu and Co/Ag nanoparticles stabilized by chitosan were determined. The polydispersity index and the diameter of nanoparticles were observed to decrease in contrast to the original polymer during the creation of chitosan stabilized bimetallic nanoparticles, decreasing from 0.342 to 0.12±0.04 and 2.5 micron to 180 nm, respectively. However, the diffusion coefficient of chitosan was increased from 0.2 cm^2/s to 2.71 cm^2/s during the production of stable bimetallic nanoparticles. The lack of absorption bands at 500 nm and 700 nm-900 nm in the UV spectra of the samples suggests that in the presence of a reducing agent, copper (II) and cobalt (II) ions undergo full reduction. The relationship between the synthesis conditions and the kind of structure of bimetallic nanoparticles "core-shell" has been discovered. Silver atoms have been shown to be both a core and a shell, depending on the synthesis conditions and chemical nature of metal ions.

1. Introduction

Different metal atoms create bimetallic nanoparticles (BNPs) and/or heteronuclear metal complexes, which have better mechanical and catalytic performance than monometallic complexes due to their synergistic functionalities and their intriguing biological and operational features, bimetallic complexes, particularly BNPs, have lately gained a lot of interest [1-4]. In this sense, there has lately been a trend toward using bimetallic compounds in relation to their potential in medicine. In a bimetallic complex, each metal center contributes according to its chemical characteristics, resulting in a boost in the complex's antibacterial capabilities above its monometallic counterpart.

BNPs are complexes with qualities that are significantly superior to those of their constituents. The usage of noble metals and the first-row transition value, in particular, are gaining popularity for applications in catalysis, electrocatalysis, and magnetism. Because of their capacity to form intermetallic phases, random alloys, and core-shell species, such objects have a diverse structural chemistry. Under impact on the surface, however, the nanostructure can be altered due to the observation, segregation, or

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isolation of many atoms, resulting in the formation of a structure with higher catalytic activity [5].

In comparison to metallic nanoparticles, the production, physicochemical characteristics, and uses of bimetallic nanoparticles based on noble and transition metals are now intensively addressed. As a result, BNPs outperform their metallic counterparts in terms of biological, chemical, and mechanical qualities. BNPs Au/Ag, Ni/Pd, Au/Pd, and Au/Pt in the size range of 1 nm-100 nm have been reported to find specialized uses in diagnostics (bioimaging), biosensors, treatment, and drug delivery systems as a result of these features [6-8]. The size and distribution of bimetallic nanoparticles, shape, the ratio of two metals, and the internal distribution of metals in individual nanoparticles, for example, the presence of homogeneous alloys, core-shell systems, and other types of bimetallic nanoparticles are all important parameters for characterization [6].

One of the most essential features of their utilization is the fabrication of nanostructure catalysts based on bimetallic nanoparticles. It's probable that the synergistic impact of BNPs, in which they're interlinked at the atomic level and create diverse structures like alloys, core-shells, heterodimers, and so on, is linked to the effectiveness of bimetallic catalysts. The kinetics of catalysis can be affected by variations in the electronic state of metal centers in such materials [7].

As a result, BNP structure may be split into two categories: mixed structures and segregated structures. BNPs may be classified into four categories based on their atomic ordering: alloys, intermetallic compounds, subclusters, and shell-cores (core-shells, materials with several cores covered with one shell). BNP structures are created when two distinct elements are combined with a random mechanism of dispersion or nuclear envelope creation, such as mixed and random alloys, subclusters with two, three, or a small number of A-B bonding interfaces, and core-shell type at others [8-10].

The researchers created spherical bimetallic Ag/Fe nanoparticles of the "core-shell" type with a diameter of 136.3 nm that were bactericidal against multiresistant bacteria. It was discovered that BNPs Ag/Fe had better bioactivity against yeast and gram-positive and gram-negative bacteria than silver and iron mono-NPs. The link between "structure-bactericidal activity" and the prevention and treatment of infections caused by clinically important drug-resistant strains has been demonstrated [11].

Metal-containing nanomaterials, such as mono- and bimetallic nanoparticles, oxide nanoparticles with bioactive qualities that range in composition and properties, are currently in high demand in the nanoindustry [12-14]. BNPs appear to be crucial and promising nanomaterials in catalysis, medicine, agriculture, photocatalysis, and other fields. They differ from one other in composition and structure, as well as core-shell type, composition and structural dependent properties. Nanomaterials, including Pd/Co, Pd/Ru, Pd/Au, Pd/Fe, Au/Pt, Au/Pd, Cu/Ag, Co/Rh, Pd/Pt, Cu/Fe, Ag/Fe, Ni/Cu, and others, have been obtained in this vein [15-23].

The impact of BNP structure on their physicochemical and operational qualities, as well as the creation of a link between the synthesis technique and structure, are both basic and practical research topics. In this context, the discovery of ways for producing bimetallic NPs and stabilizing them, as well as the identification of potential applications, is of critical practical importance.

2. Materials and Methods

ChS *Bombyx mori*, with a molecular mass of 200×10^3 and a degree of deacylation of 70%, was employed to make stabilized bimetallic NPs. Metal salts such as $CoCl_2$, $CuSO_4$ and $AgNO_3$ were utilized because they were "chemically pure".

The kinetic parameters were investigated using a Litesizer 100 device (Anton Paar GmbH, Austria), which is used to calculate particle size using the Einstein-Stokes equation's diffusion coefficient. A single frequency laser diode with a 40 mW output produces a 658 nm laser.

The method of static and dynamic light scattering (photon correlation spectroscopy) - DLS - was used to measure the size of composites. The range of measured dimensions is in the range from fractions of nm to 5-10 microns. The power of the analyzer's laser is in the range of 2 mW-35 mW. Photocor analyzers have a mode of automatic measurements, processing and presentation of analysis results.

A SPECORD 210 spectrophotometer was used to conduct UV spectroscopic experiments in the range of 190 nm-1000 nm. Photometry UV accuracy using potassium dichromate according to Ph. Eur. 0.01.

3. Results and Discussion

The approach [14] was used to make chitosan-stabilized bimetallic nanoparticles (BNPs) in the presence of a reducing agent, $NaBH_4$. Metal ions were totally reduced and their number was 5±0.5% for all samples, according to the findings of spectral analysis of the mass fraction of metals.

3.1 The Studies the Kinetic Parameters of BNPs - Cu/Ag and Co/Ag

The hydrodynamic dimensions, diffusion coefficients, and polydispersity index of chitosan stabilized bimetallic nanoparticles have all been determined (Table 1).

Table 1. The effect of synthesis time on the particle size of chitosan stabilized bimetallic particles. 2.5 micron d (ChS)

#	BNPs samples	$[NaBH_4]\times10^{-4}$, mol	d, nm				Δd, nm
			3 min	6 min	9 min	12 min	
1	Cu^{2+}/Ag^{+}=2:1	1.3	227	235	231	224	230
2	Cu^{2+}/Ag^{+}=2:1	2.0	186	182	177	179	180
3	Cu^{2+}/Ag^{+}=2:3	2.0	246	264	267	260	260
4	Co^{2+}/Ag^{+}=1:1	2.6	199	218	212	200	207

The size of polymer-stabilized nanoparticles falls by around 10 times the size of polymer macromolecules during the synthesis of bimetallic nanoparticles in the presence of chitosan, according to studies of the hydrodynamic diameters of BNPs. The data also show that BNPs develop quickly, since the particle diameter does not vary from 3 to 12 minutes in any of the systems studied, and the average particle diameter is 180 nm-270 nm. It should be mentioned that the polydispersity indices in all of the examined systems of polymer-stabilized Me^{2+}/Ag^{+} BNPs are close to each other and, as a result, fall from 0.342 to 0.12±0.04 (Table 2).

This might be attributed to the disruption of intramolecular and intermolecular H-H and electrostatic bonds in chitosan solutions, as well as participation in metal nanoparticle stabilization. The data obtained from the DLS measurements are also close to the Litesizer results and range from 0.296 to 0.338.

As a result, it was discovered that the value of the diffusion coefficient of chitosan reduces by around 10 times after the stabilization of bimetallic nanoparticles. Furthermore, it was shown that the diffusion coefficient of chitosan stabilized bimetallic NPs is inversely related to the polydispersity index and particle diameter. Over example, the results in Table 3 show that for 3-12 minutes, the values of the diffusion coefficient of the particles of the tested samples are almost the same. DC sample #2 has a comparatively high flow rate of 2.71 cm^2/s, and the IP=0.12±0.04 and d=180 nm particle sizes are tiny, respectively.

The study of the prolongation effect of polymeric materials on drugs is of particular interest, which can be evaluated by modern physical methods [24]. The UV spectroscopy method has been used to study the kinetics of the release of ChS particles stabilized by BNP from the film, in which the absorption intensity is directly proportional to the number of electronic transitions or the concentration of the substance under study. The kinetics of this process can be considered as the diffusion of particles into an aqueous medium accompanied by conformational transitions of the polymer matrix leading to dissolution (Figure 1a,b).

Table 2. The effect of synthesis time on the index polydispersity (IP) of chitosan stabilized bimetallic particles. 0.342 IP (ChS)

#	BNPs samples	index polydispersity				ΔIP (by Litesizer)	IP (by DLS)
		3 min	6 min	9 min	12 min		
1	Cu^{2+}/Ag^{+}=2:1	0.25	0.16	0.18	0.21	0.20±0.04	0.314
2	Cu^{2+}/Ag^{+}=2:1	0.14	0.08	0.16	0.16	0.12±0.04	0.296
3	Cu^{2+}/Ag^{+}=2:3	0.23	0.19	0.26	0.26	0.22±0.03	0.326
4	Co^{2+}/Ag^{+}=1:1	0.11	0.15	0.21	0.25	0.18±0.06	0.338

Table 3. The effect of synthesis time on the diffusion coefficient (DC) of chitosan stabilized bimetallic particles. 0.2 cm^2/s DC (ChS)

#	BNPs samples	diffusion coefficient				ΔDC, cm^2/s
		3 min	6 min	9 min	12 min	
1	Cu^{2+}/Ag^{+}=2:1	2.16	2.08	2.11	2.18	2.13
2	Cu^{2+}/Ag^{+}=2:1	2.63	2.70	2.76	2.73	2.71
3	Cu^{2+}/Ag^{+}=2:3	2.47	2.25	2.31	2.45	2.37
4	Co^{2+}/Ag^{+}=1:1	1.99	1.85	1.83	1.88	1.90

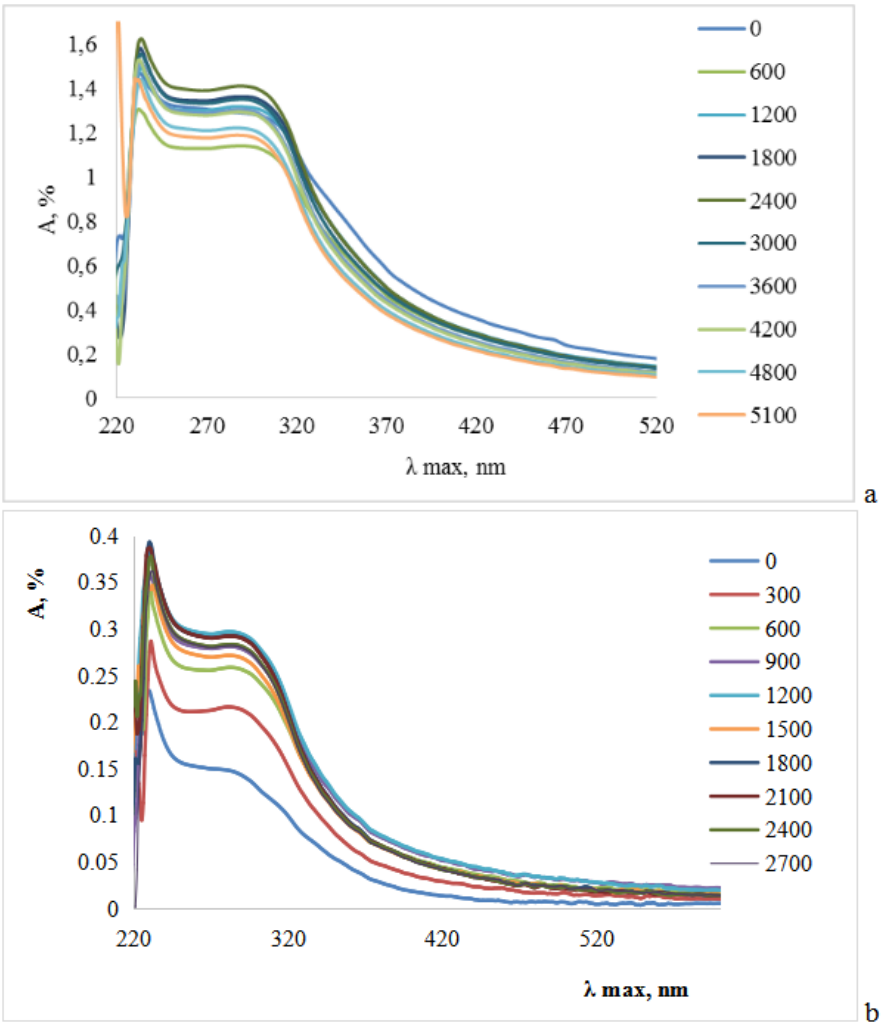

Figure 1. UV spectra of the release kinetics of chitosan stabilised bimetallic nanoparticles from the film of samples 3 (a) and 4 (b) with an interval of 10 minutes

Based on the results of the study, the diffusion coefficient of the BNP release process from the film in a medium of 2% CH_3COOH was estimated. To estimate the diffusion coefficient, we used the formula described by Fick's second law, which is given below:

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \quad (1)$$

$$c(x,t) = \frac{A}{\sqrt{t}}\exp\left(\frac{-x^2}{4Dt}\right) \quad (2)$$

where c is the concentration of the solution, t is time, and D is the diffusion coefficient.

It follows that during the diffusion of polymer-stabilized BNP in an acidic medium there is a change in the intensity of the optical density of the solvent - CH_3COOH, which is directly proportional to the concentration of the dissolved substance. Fixing the change in absorption intensity over time of diffusion into the solvent, we determined the diffusion coefficients for samples #3 and #4, which are 2.723×10^{-7} cm^2/s and 4.817×10^{-8} cm^2/s, respectively.

3.2 UV Spectroscopic Studies

In order to research the structure of chitosan stabilized BNPs, we carried out UV studies (Figures 2 and 3).

The absorption bands of copper (II) ions are entirely decreased at 700 nm-900 nm in the spectra of the samples ChS-Cu/Ag examined. Cu NPs, on the other hand, generate a wide absorption band at 200 nm-300 nm that coincides with the absorption bands of chitosan's amin and acetamide groups. It's worth noting that the absorption band at 425 nm, which is typical of Ag NPs, is only seen in the spectra of sample #1. This might imply that Ag NPs are on the exterior of the sample, acting as a shell, where-

as Cu NPs comprise the center. The absorption bands of Ag NPs are not evident in samples #2 and #3, despite the fact that the quantity of NPs is 5%. Ag NPs are most likely the center of these samples, with Cu NPs forming a shell around them.

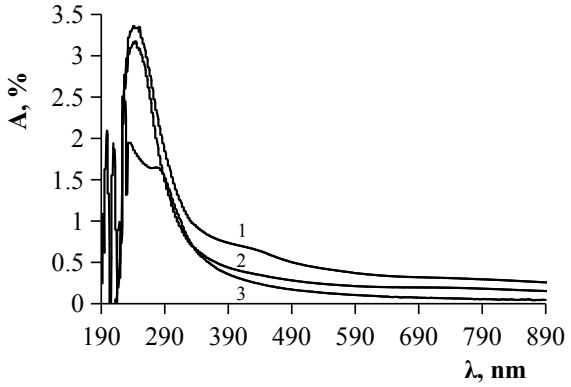

Figure 2. UV-spectra of ChS stabilized BNPs Cu/Ag: (1) Cu^{2+}/Ag^{+}=2:1, $[NaBH_4]$: 1.3×10^{-4} mol; (2) Cu^{2+}/Ag^{+}=2:1, $[NaBH_4]$: 2.0×10^{-4} mol; (3) Cu^{2+}/Ag^{+}=2:3, $[NaBH_4]$: 2.0×10^{-4} mol

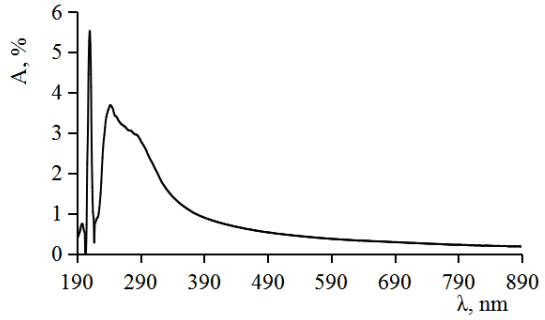

Figure 3. UV-spectra of ChS stabilized BNPs Ag/Co: Co^{2+}/Ag^{+}=1:1, $[NaBH_4]$: 2.6×10^{-4} mol

There is no absorption band of cobalt (II) ions at 500 nm in the spectra of sample #4, nor is there an absorption band of Ag NPs at 275 nm-600 nm. However, at 200 nm-206 nm, a significant absorption band develops, which is characteristic of Co NPs. This is most likely owing to the fact that spherical BNPs are generated under the specified synthesis conditions, with Ag NPs in the core and Co NPs in the shell. The results are consistent with those seen in the literature [15].

4. Conclusions

In conclusion, the hydrodynamic characteristics of chitosan stabilized bimetallic NPs - Cu/Ag and Co/Ag - produced under different synthesis circumstances have been determined. It has been discovered that the hydrodynamic properties of BNPs do not change significantly between 3 minutes to 12 minutes. A link has been established between the diffusion coefficient values and the polydispersity index, as well as the diameters of stabilized bimetallic nanoparticles.

Conflict of Interest

There is no conflict of interest.

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