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PHYSICOCHEMICAL STUDIES OF COTTON CELLULOSE AND ITS DERIVATIVES CONTAINING SILVER NANOPARTICLES

Kh. E. Yunusov,* A. A. Atakhanov, N. Sh. Ashurov,
A. A. Sarymsakov, and S. Sh. Rashidova

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The shape, number, and size of silver nanoparticles contained in cotton cellulose and its derivatives were studied using x-ray diffraction, atomic absorption spectroscopy, transmission electron microscopy, and elemental analysis. Silver nanoparticles in sodium carboxymethylcellulose were smaller and more numerous and had a more even distribution than those in cotton and microcrystalline cellulose. The size and shape of silver nanoparticles depended on the nature of the polymer matrix.

Keywords: cotton cellulose, microcrystalline cellulose, silver nanoparticles, sodium carboxymethylcellulose, silver crystallites.

Ultradispersed metals exhibit unusual properties that open new possibilities for their practical application. Silver nanoparticles, which are an antimicrobial agent, are especially interesting. Several methods for producing stable metal nanoparticles, including chemical, biochemical, physical, and others, are known.

The synthesis of metal clusters and nanoparticles in polymer solutions and matrices is a vigorously developing area for preparing nanostructured metal-containing systems with an array of unusual physicochemical properties [1].

Research in this area indicates that macromolecules not only stabilize dispersed systems but also participate directly in their formation by controlling the size and shape of the growing nanoparticles [2]. The use of natural polymers as the polymer matrices for growing metal nanoparticles is even more attractive because they can undergo biodegradation.

Therefore, it seemed promising to study the structures and properties of cotton cellulose derivatives containing silver nanoparticles. We studied previously the ability to prepare silver nanoparticles in matrices of cellulose derivatives and showed that the resulting materials acquired new, in particular bactericidal, properties that were uncharacteristic fon the starting materials [3].

The goal of the present work was to study cotton cellulose derivatives (microcrystalline and carboxymethylated cellulose) containing silver nanoparticles using physical and physicochemical methods.

X-ray diffraction studies showed (Fig. 1) that carboxymethylcellulose (CMC) had an amorphous structure and gave a diffuse ring at $2\theta = 21.6°$. CMC containing silver ions also had an amorphous structure with a weaker ring in the same region. Two phases were found in diffraction patterns of polymeric CMC composite with reduced silver nanoparticles. These corresponded to amorphous CMC at diffraction angle $2\theta = 21.6°$ and metallic silver. Silver with a cubic crystal lattice and $a = 4.086$ Å gives reflections at $2\theta = 38°$, 44°, 65°, and 78° from planes (111), (200), and (220) [4].

The size of the silver crystallites was calculated from the peak widths. The width of x-ray diffraction peaks is known to depend on the size of the crystallites and their coherent scattering regions. The greater the size of these regions is, the narrower the reflection in the x-ray pattern. The effective crystallite sizes were determined using the Scherrer formula and the width of each line.

The effective size of the silver crystals in the CMC matrix was 15 nm according to the calculations.

Figure 2 shows high-angle reflections in the x-ray pattern of starting microcrystalline cellulose (MCC) containing silver cations and silver nanoparticles. Starting MCC had characteristic reflections around 22.75° that belonged to the reflection from the (200) plane.

Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, Tashkent, e-mail: haydar-yunusov@rambler.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 370–373, May–June, 2011. Original article submitted October 4, 2010.

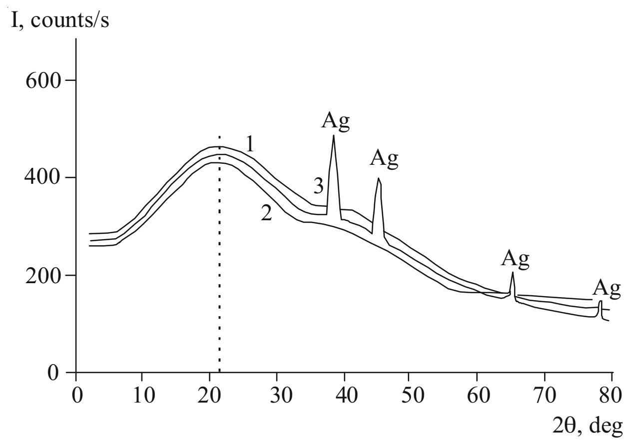

Fig. 1

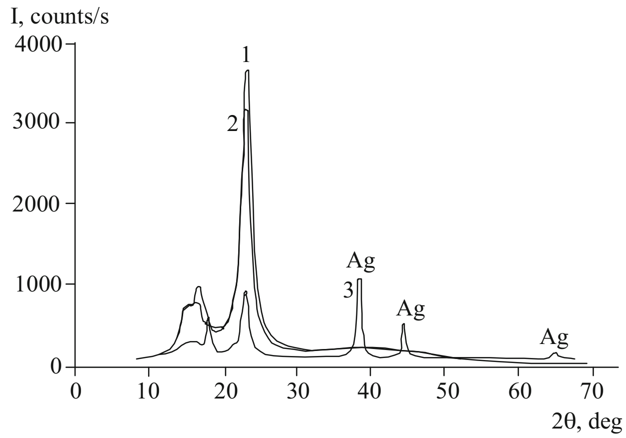

Fig. 2

Fig. 1. Diffraction patterns of starting CMC (1), CMC containing Ag cations (2), and CMC containing silver nanoparticles (3).
Fig. 2. Diffraction patterns of starting MCC (1), MCC containing Ag cations (2), and MCC containing silver nanoparticles (3).

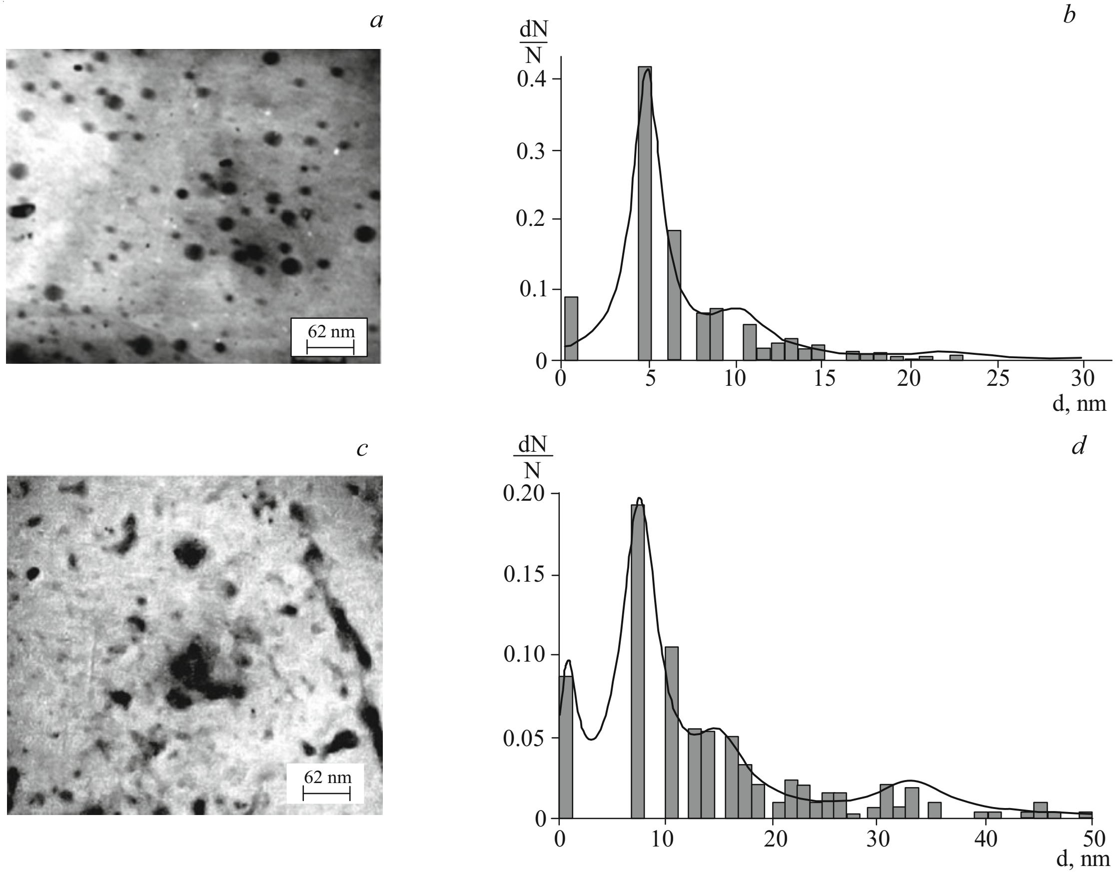

Fig. 3. TEM images (a, c) and particle-size distributions (b, d) for CMC + Ag^0 (a, b) and MCC + Ag^0 (c, d).

The study of MCC samples containing silver nanoparticles showed that the degree of crystallinity and the intensity of the crystal reflections of MCC containing silver nanoparticles were less than those of starting MCC and MCC containing Ag cations. It was possible that this was due to the fact that Ag^+ ions penetrated the crystalline part of MCC upon mixing the $AgNO_3$ solution with the aqueous suspension of MCC and UV radiation produced atomic Ag that then formed larger clusters. This process destroyed intermolecular bonds of the supramolecular structure, reducing the degree of MCC crystallinity. Crystal reflections at $2\theta = 38°$, 44°, and 65° belonged to silver crystallites, were clearly visible, and had effective size 20 nm (Fig. 2).

The size of the silver nanoparticles in the polymer matrix was calculated from the x-ray diffraction patterns.

TABLE 1. Atomic Absorption and Elemental Analyses of Silver-Containing Nanocomposites Based on CMC and MCC, %

Sample	Ash analysis		Atomic absorption analysis		Elemental analysis				
	Ash	Ag, in ash	Na	Ag	Na	C	H	Ag	O
CMC	8.41	–	5.36	–	6.84	28.85	2.65	–	61.66
CMC + Ag^0	10.45	3.14	–	3.04	6.41	28.85	3.08	2.43	61.23
MCC	8.41	–		–		43.65	6.03	–	50.32
MCC + Ag^0	10.45	1.04		0.75		32.82	3.22	0.68	63.28
Theoretical									
CMC	–	–	–	–	9.54	37.83	4.14	–	48.49
CMC + Ag^0		3.24	–	3.24	8.43	39.44	3.06	3.24	47.64
MCC		–		–		44.44	6.17	–	49.39
MCC + Ag^0	–	3.24		3.24		44.26	4.22	3.24	48.28

The size of the silver nanoparticles was in the range 8.5 nm [from plane (111)], 13.7 [from (200)], and 32.7 [from (220)] for CMC and 31.1 nm [from (111)], 34.1 [from (200)], and 41.8 [from (200)] for MCC, i.e., the size of the silver nanoparticles depended on the nature of the polymer matrix.

Transmission electron microscopy showed (Fig. 3a) that the silver nanoparticles were spherical. However, their size depended on the polymer matrix.

UV irradiation of CMC-Ag^+ and MCC-Ag^+ produced various physical processes that affected the size and shape of the resulting silver nanoparticles. The x-ray patterns showed that CMC was amorphous and formed a genuine homogeneous aqueous solution whereas MCC consisted of fibrillar crystallites that were insoluble in water. However, MCC formed a stable suspension in water that affected the penetration of the UV radiation.

This agreed well with experimental results because silver nanoparticles with a narrow particle-size distribution and small particle sizes were formed by UV irradiation of the complex $CMC^-{\cdot}Ag^+$. This was due to the carboxylate group, which acted as a nanoreactor [5] and created conditions that were favorable for reducing and stabilizing silver nanoparticles. Irradiation of $MCC{\cdot}Ag^+$ produced an intensity gradient of UV radiation in the suspension. This produced relatively large silver nanoparticles with a broad particle-size distribution. The scatter in the particle-size distribution of silver nanoparticles was small for CMC and had a Gaussian shape. The dominant particle size was 5 nm with a minimum size of 1 nm and a maximum size of 20 nm (Fig. 3b).

Larger silver nanoparticles with a greater particle-size distribution formed if MCC was used as the polymer matrix. The dominant size was about 7 nm with a maximum size reaching 50 nm (Fig. 3d).

A study of the morphology showed that CMC was the more favorable matrix for preparing silver nanoparticles with smaller sizes and a more homogeneous size distribution. The size and shape of metal nanoparticles depended on several factors such as the nature of the polymer, the degree of polymerization, the degree of substitution, etc. The lower the degree of polymerization and the higher the degree of substitution are, the greater the probability of producing nanoparticles with a spherical shape and the smallest metal-particle size.

Atomic absorption spectroscopy and elemental analysis showed that the silver content was an order of magnitude greater if CMC was used as the polymer matrix rather than MCC. This proved our hypothesis that CMC was a more favorable polymer matrix for forming silver nanoparticles because of the carboxylate ions (Table 1).

Table 1 shows that the contents of silver nanoparticles in CMC as determined by ash and atomic absorption spectroscopy were rather similar. The silver content determined by elemental analysis was slightly less. This was explained by the multiple steps and low accuracy of the method.

This method consisted in essence of dissolving in water CMC samples containing silver nanoparticles and determining gravimetrically after precipitation as silver chloride the amount of unreduced silver ions. The content of silver nanoparticles was calculated from the content of silver ions in CMC before and after UV irradiation.

Table 1 presents the contents of silver nanoparticles in MCC that were determined by different methods. It can be seen that the content of silver nanoparticles in MCC was much less than in CMC. This was explained by the fact that UV radiation was reflected from MCC particles on passing through the MCC suspension containing silver ions. This reduced the efficiency of the photoreduction of silver ions by 67–75%.

The detailed formation mechanism of rod-shaped silver nanoparticles (30–45 nm) in the MCC suspension remains unclear and requires further research.

Thus, the physicochemical properties of cotton cellulose derivatives containing silver nanoparticles were studied. X-ray diffraction analysis showed that production of silver nanoparticles in the polymer matrix made the polymer structure amorphous. The size of the silver crystallites in the polymer matrix was calculated to be in the nanometer range, from 1 to 20 nm for CMC and from 1 to 50 nm for MCC.

Electron microscopy studies showed that the size and shape of the silver nanoparticles depended on the nature of the polymer matrix. Larger and rod-shaped silver nanoparticles (Fig. 3c and 3d) with a broad particle-size distribution formed if MCC was used as the polymer matrix.

The silver nanoparticles were uniform in shape (spherical) (Fig. 3a and 3b) with a narrow particle-size distribution if CMC was used.

EXPERIMENTAL

Silver-containing nanocomposites with the natural polymers MCC and CMC as the polymer matrix were used for the studies.

The phase composition of the samples was studied by x-ray diffraction analysis on a DRON-3M diffractometer.

The morphology of the nanometal–polymer surface layers was studied using a PEM-100 transmission electron microscope. The average particle size of the metal in the polymer matrix and the variation coefficient were determined by the appropriate calculations using the program Sigma Scan Pro 5. The silver content in the nanocomposites was determined by elemental analysis and atomic absorption spectroscopy on a Perkin–Elmer (USA) 3030 B spectrophotometer with a flame analyzer (acetylene–air).

Absorption was measured at wavelength 338.3 nm in the UV range corresponding to Ag^0.

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