

# Atomic Force Microscopy and X-Ray Photoelectron Spectroscopy Study of Chitosan–Carbon Fiber Materials

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**Abstract**—Chitosan–carbon materials produced by electrochemical deposition of chitosan on an activated carbon fiber (ACF) as an electrode have been studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). AFM data demonstrate that the microstructure of the coating depends on whether chitosan is deposited in soluble or insoluble form. XPS data are used to evaluate the state of chitosan in the composites in relation to the deposition conditions.

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## INTRODUCTION

Carbon fibers (CFs) and carbon fiber materials (CFMs) stand out among the many types of chemical fibers because of the great diversity of their applications. They are used as reinforcing agents of polymer-, ceramic-, carbon-, and metal-matrix composites and in electrical batteries and energy storage devices such as supercapacitors. Surface-modified CFs are used to produce materials with ion-exchange properties [1–4].

The surface condition of CFs, namely, their pore structure and surface functional groups (SFGs), determines the characteristics of the fiber and related composites.

The quantitative and qualitative composition of SFGs influences the sorption behavior of CFMs, as observed in extraction of various substances, e.g., metals and organic compounds. SFGs can be produced by surface oxidation of fibers: gas- or liquid-phase chemical oxidation or electrochemical oxidation in various electrolyte solutions. The composition of functional groups forming on the surface of CFMs depends on the oxidation procedure [5–8].

One fiber-surface modifier potentially attractive for designing sorbents alternative to synthetic ion exchangers is chitosan, poly- $\beta$ -(1 $\rightarrow$ 4)-*N*-acetyl-*D*-glucosamine, a natural biopolymer resulting from partial

deacetylation of chitin and containing hydroxyl, amino, and acetylamide groups, oxygen bridges, and other functional groups. Chitosan possesses pH-dependent solubility (Fig. 1), because the apparent dissociation constant of the conjugate acid is  $pK_a \approx 6.5$ – $6.7$ , and dissolves in water only at  $pH < 6$ . Owing to this property, it can be used to produce composite sorbents with films of various compositions on the surface of CFs via electrochemical modification using conducting CF as an electrode [9].

In this paper, we describe new sorbent materials based on activated carbon fibers (ACFs) surface-modified via electrochemical polarization of CFs in chitosan solutions. The purpose of this work was to study the surface condition of chitosan–carbon materials (CCMs) by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) in relation to the fabrication conditions (electrode potential and heat-treatment temperature) of the composites.

## EXPERIMENTAL

**Starting materials.** In our preparations, we used Aktilen B ACF braids (Len-NII Khimvolokno). Their specific surface area (determined by BET analysis of nitrogen adsorption isotherms), pore volume, and average

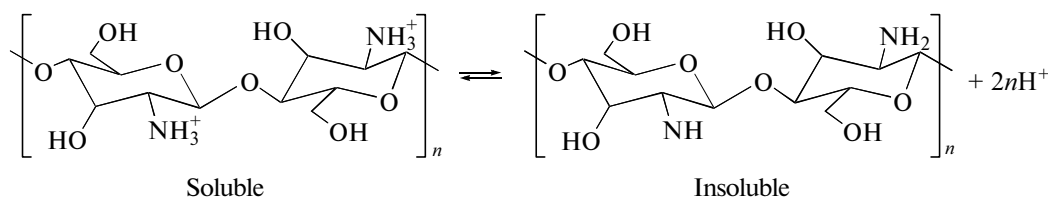


Fig. 1. Structure of chitosan.

pore radius were 700 m<sup>2</sup>/g, 0.4 cm<sup>3</sup>/g, and 0.4 nm, respectively. The fibers were first washed with distilled water under sonication. Fiber materials were modified with high-molecular chitosan manufactured by ZAO Vostok-Bor (Purity Standard TU 9289-092-00472124-99).

**Fabrication of composite sorbents.** Chitosan–CFM composite sorbents were prepared through electrochemical processing of CFMs in a dilute solution of chitosan in hydrochloric acid in the presence of sodium chloride. The fiber material was used as a cathode or anode and was polarized to a certain potential and held at this potential for a predetermined time (3–4.5 h) in order to deposit chitosan on the fiber surface [9]. In what follows, sample designations include the electrochemical processing potential (mV) in parentheses.

To assess the temperature effect on the characteristics of the composites, we used CCM(–900) and the same composite heat-treated at 100–120°C: CCM(–900)-*T*.

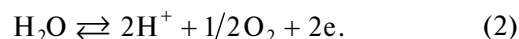
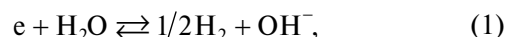
**Sample characterization.** The surface morphology and texture of the composite materials were examined by AFM on a SOLVER instrument (OAO NT-MDT, Zeleograd).

Core-level XPS spectra were measured on an ES 2401 electron spectrometer (Russia) with unmonochromatized ALK<sub>α</sub> radiation. The vacuum in the sample analysis chamber was maintained at 10<sup>–5</sup> Pa. The spectra of the high-molecular chitosan were calibrated using the C 1s level (*E*<sub>b</sub> = 285.0 eV) arising from the saturated carbon contamination on the sample surface. The C 1s binding energy in the ACF, a conducting material, was measured from the Fermi level of the spectrometer material. The value obtained, 284.8 eV, was used as the energy-scale reference for the C 1s level of the carbon matrix of the chitosan-modified ACF samples. In determining the relative element concentrations, we took into account the photoelectron escape direction, transmission function of the analyzer, wave function asymmetry, and Scofield's core-level photoionization cross sections [10]. Our calculations thus utilized “reduced” integrated intensities that took into account the above factors. Element concentrations were expressed as a percent of the total carbon content. The measured spectra were decomposed into elementary components using the XPSPEAK 4.1 (free download) program.

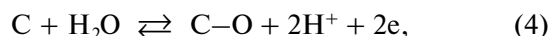
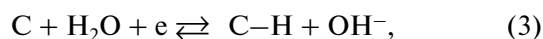
## RESULTS AND DISCUSSION

When CCM samples are prepared in the cathodic potential region, chitosan deposits on the CF surface in its insoluble form due to its ability to deposit in alkaline media. At open-circuit potentials in the anodic potential region, chitosan adsorbs on the CF surface. In the anodic potential region, the CFM may experience partial oxidation, leading to the formation of additional oxygen-containing groups on the CF surface. The composite may then contain both amino groups (including protonated groups) of chitosan and various oxygen-containing groups [9]. This is because the SFGs of the electrode (as-prepared or chitosan-modified ACFs) are involved in

redox or ion-exchange reactions with the participation of hydroxonium or hydroxyl ions. Additional surface processes (besides chitosan deposition) are caused by two reactions due to the electrodecomposition of water:



Since the hydrogen and oxygen are sorbed by CFs, these reaction schemes can be written in the form



where C represents the surface of the carbon material [11].

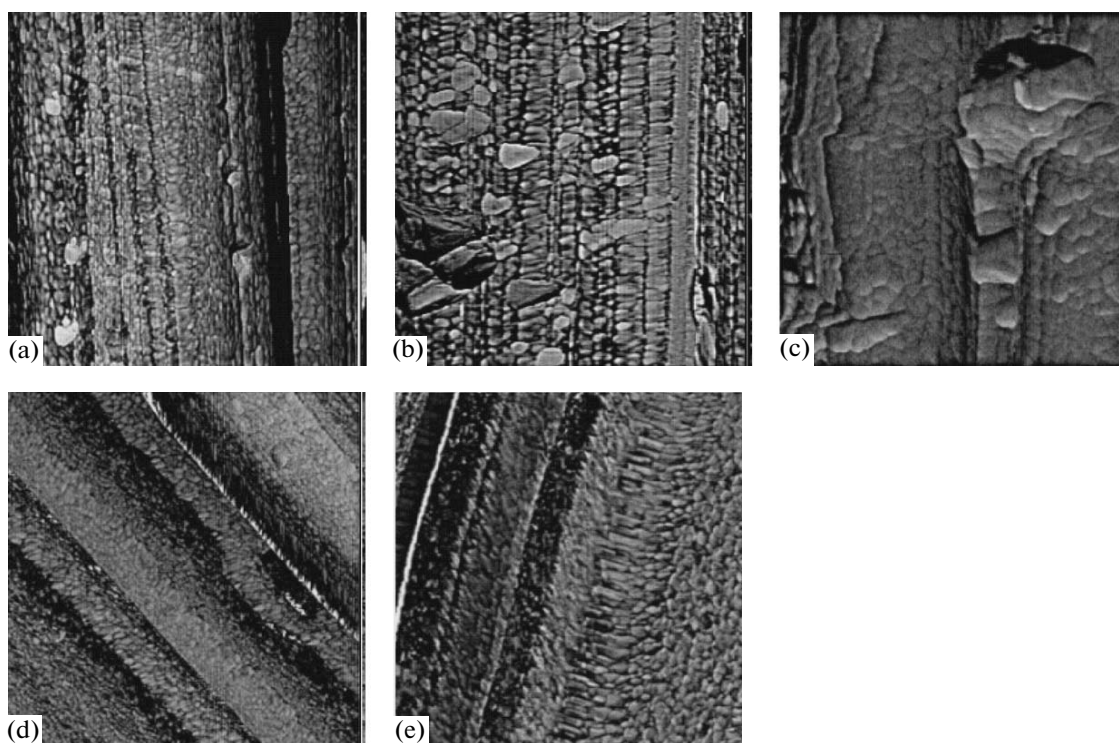
Figure 2 shows AFM images of ACFs modified with chitosan deposited in its insoluble form, CCM(–900) (Fig. 2c), and in its protonated form, CCM(OC) and CCM(+900) (Figs. 2d, 2e). Note that the displacement of the CFs in the CCM(–100) sample (Fig. 2b) compared to the as-prepared fibers (Fig. 2a) is fixed by the insoluble chitosan film in the initial stage of its growth.

Figure 3 compares AFM images of CCM(–900), CCM(–900)-*T*, and as-prepared ACFs. The AFM data attest to shrinkage of the chitosan film in the heat-treated sample and the formation of numerous pores 10–12 nm in diameter.

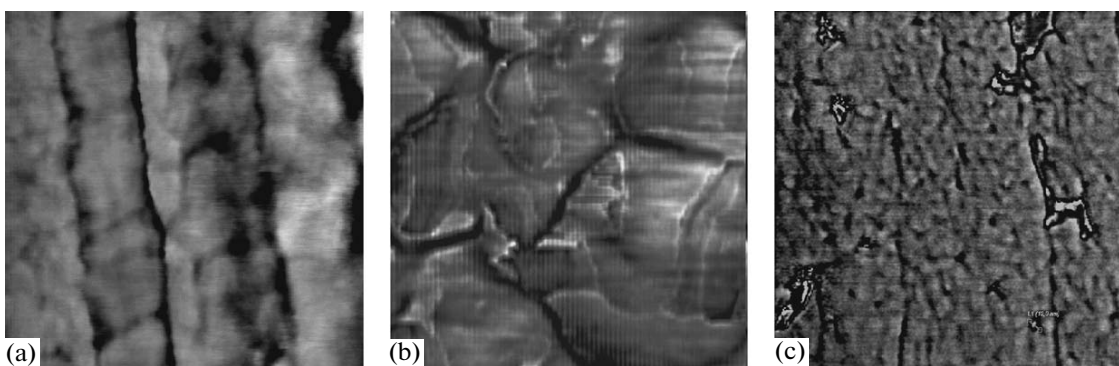
The possible formation of additional oxygen-containing groups (at anodic potentials) or their breakdown as a consequence of electrochemical cathodic processing and the possible changes in the coating (chitosan) on the surface of CFs during heat treatment were assessed from the changes in the *E*<sub>b</sub> of the C 1s, O 1s, and N 1s levels and semiquantitative estimates of the concentrations of the main chemical elements.

The XPS spectra of chitosan are presented in Fig. 4a. Components *A* (286.1 eV), *B* (286.7 eV), and *C* (288.4 eV) in the C 1s spectrum are due to carbon atoms bonded to the nitrogen of amino groups, one oxygen, and two oxygens, respectively. Their relative integrated intensities are consistent with the idealized structure of the polymer unit in fully deacetylated chitosan (Fig. 1). Peak *D* arises from the saturated carbon contamination on the sample surface. The N 1s spectrum in Fig. 4a shows an additional component shifted by ≈1.6 eV to higher *E*<sub>b</sub> values relative to the main signal, which indicates that some of the amino groups are protonated. The O 1s spectrum shows, in addition to the main peak, O(I), at *E*<sub>b</sub> = 532.9 eV, weak components O(II) (531.5 eV) and O(III) (534.3 eV). Veleshko et al. [12] attributed the low-energy component in the O 1s spectrum of chitosan to –OH<sup>–</sup> groups. The O(III) peak seems to arise from sorbed water.

Figure 4b shows the 1s spectra of the as-prepared ACFs. Component *M* is due to the carbon matrix and comprises the signals from the *sp*<sup>2</sup> carbon, aliphatic fraction, and π → π\* transitions. The weak C 1s features at *E*<sub>b</sub> = 286.4 and 288.3 eV are due to the carbon singly bonded to oxygen and to the carbon of carbonyl



**Fig. 2.** AFM images of activated CFMs: (a) as-prepared, (b) CCM(-100), (c) CCM(-900), (d) CCM(OC) (open-circuit potential), and (e) CCM(+900); scan area  $2.5 \times 2.5 \mu\text{m}$ .



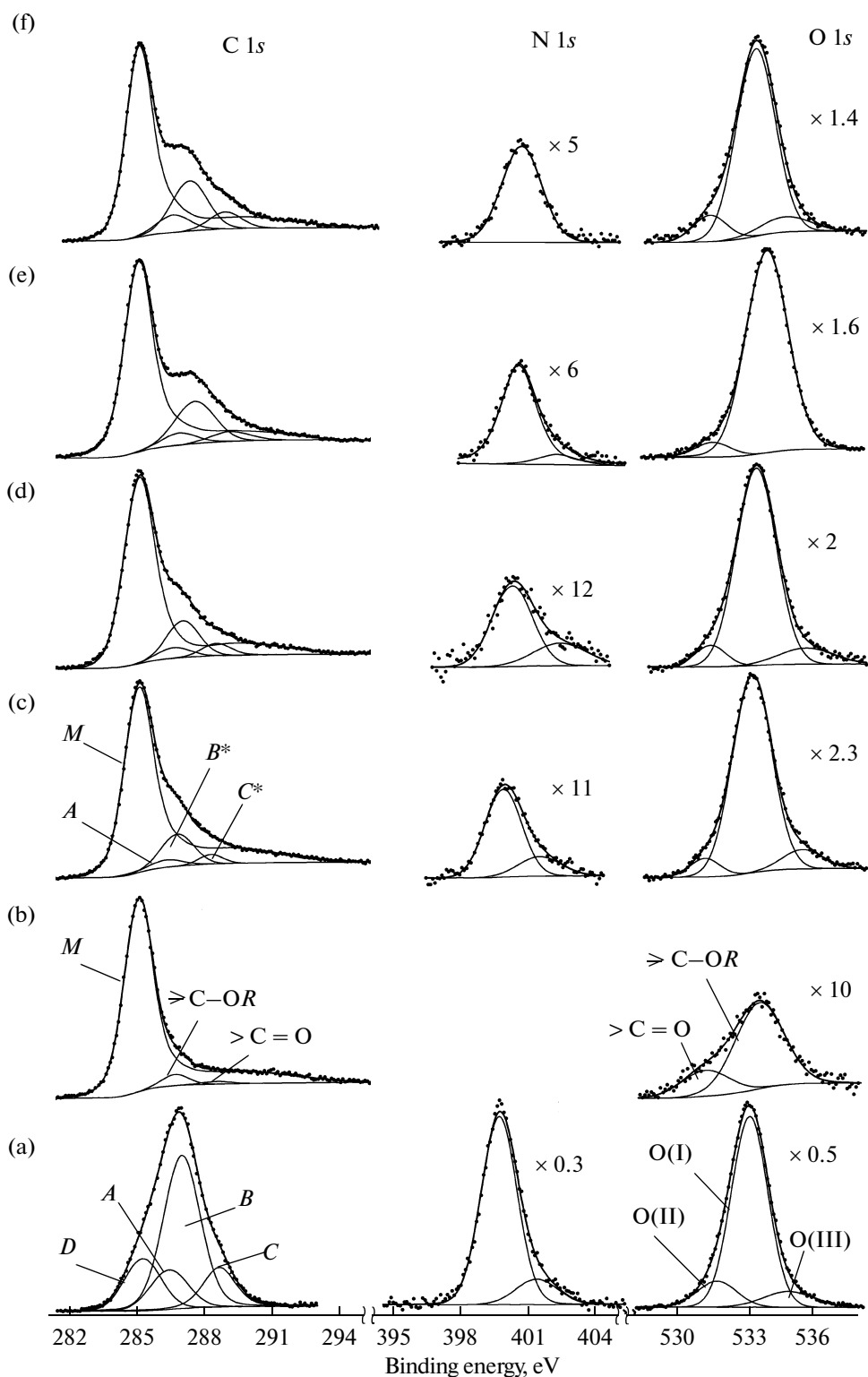
**Fig. 3.** AFM images of surface areas of (a) as-prepared ACFs, (b) CCM(-900), and CCM(-900)-*T*; scan area (a, c)  $350 \times 350$  and (b)  $450 \times 450$  nm.

groups, respectively. Their integrated intensities correlate with the “reduced” integrated intensities in the O 1s spectrum of the ACFs (Fig. 4b). The total oxygen content on the fiber surface is  $\approx 4\%$ .

Figures 4c–4e show the measured C 1s-, O 1s-, and N 1s spectra of the ACFs modified with chitosan at different electrode potentials during electrochemical processing. In decomposing the C 1s spectrum of the CCMs into elementary components, we took into account the integrated intensities of the oxygen and nitrogen peaks. The nitrogen content evaluated from XPS data can be used to estimate the amount of chitosan deposited on the surface of ACFs by different procedures. Peak *B*\* in the C 1s spec-

trum includes the signals from the carbon atoms bonded to one oxygen in chitosan and from the carbon singly bonded to oxygen in the CFMs. Component *C*\* arises from the carbon of the carbonyl groups in the matrix and the carbon bonded to two oxygens in chitosan. From the amount of oxygen in the chitosan present in the CCM samples, which can be estimated from the amount of nitrogen on the sample surface, and from the total oxygen content of the as-prepared ACFs, we conclude that no significant oxidation of the matrix in the anodic potential region occurs.

According to AFM data, the CCM(OC) and CCM(+900) samples contain significant amounts of chi-



**Fig. 4.** C 1s, N 1s, and O 1s spectra of (a) chitosan, (b) as-prepared ACFs, (c) CCM(+900), (d) CCM(OC), (e) CCM(-900), and (f) CCM(-900)-*T*; *R* = hydrocarbon radical or H.

tosan in pores (Figs. 2d, 2e). Given the binding energy scale calibration procedure used, the CCM(+900) and CCM(OC) samples differ only slightly in the position of

the C 1s peaks attributed to the chitosan on the ACF surface and to the parent chitosan, all the more because peaks *B*\* and *C*\* (Figs. 4c–4e) are multicomponent. The

$E_b$  of the O(III) peak in these samples is higher by approximately 0.6 eV, so this peak may be due not to the oxygen of water but to the oxygen involved in chitosan binding in the ACFs.

According to AFM data, owing to the formation of the insoluble form of chitosan at the electrode, the CF surface in the samples prepared via cathodic polarization is covered with a continuous chitosan layer (Fig. 2c). Estimates of changes in element concentrations from XPS data indicate that the chitosan content (based on nitrogen) of the CCM(-900) sample is approximately 50% that of CCM(+900). Given the sampling depth in this study (approximately 40–60 Å), we assume that the surface of CCM(-900) is covered with a chitosan layer 5–15 Å in thickness. The increase in the  $E_b$  of the C 1s-, O 1s, and N 1s levels in chitosan by 0.5–0.7 eV and the absence of component O(III) in the spectrum in Fig. 4e attest to changes in the interaction between the carbon matrix and chitosan. The signal from a slight amount of protonated amino groups in the N 1s spectrum is due to the fact that the insoluble form of chitosan precipitates from an acid solution, and the forming gel captures some of the acid from the solution. Heat treatment of the sample leads to a slight “reverse” shift of the chitosan peaks and causes the signal from protonated amino groups in the N 1s spectrum to disappear (Fig. 4f). One possible reason for this is that heat treatment of the CCM leads to hydrogen bond breaking and rearrangement. The O(III) component in the O 1s spectrum in Fig. 4f seems to be due to water sorption by the porous surface of the heat-treated chitosan film.

### CONCLUSIONS

We studied the interaction of chitosan with the surface of CFs during electrochemical deposition of the biopolymer. Examination of the morphology and microtexture of the CCMs showed that the electrode potential had a significant effect on the microstructure of the deposit. When chitosan was deposited in its insoluble form, the fiber surface was covered with a continuous biopolymer layer. According to XPS data, the thickness of the insoluble chitosan layer on the surface of the ACFs was 5–15 Å. Heat treatment of the sample obtained in the cathodic potential region led to dehydration of the chitosan film and the formation of numerous pores 10–12 nm in diameter.

### ACKNOWLEDGMENTS

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### REFERENCES

1. *Carbon Fibers and Their Composites*, Fitzer, E., Ed., New York: Springer, 1986.
2. Varshavskii, V.Ya., *Uglerodnye volokna* (Carbon Fibers), Moscow: Varshavskii, 2005.
3. Lysenko, A.A., Future Prospects in the Science and Technology of Carbon Fiber Sorbents, *Khim. Volokna*, 2007, no. 2, pp. 4–11.
4. De Vecchi, D.A., Moskvina, A.V., Petrov, M.L., et al., *Novyi spravochnik khimika i tekhnologa. Osnovnye svoistva neorganicheskikh, organicheskikh i elementoorganicheskikh veshchestv* (A New Chemist and Technologist's Handbook: The Main Properties of Inorganic, Organic, and Organoelemental Substances), St. Petersburg: ANO NPO Professional, 2002.
5. Yue, Z.R., Jiang, W., Wang, L., et al., Adsorption of Precious Metal Ions onto Electrochemically Oxidized Carbon Fibers, *Carbon*, 1999, vol. 37, pp. 1607–1618.
6. Chen, S. and Zeng, H., Improvement of the Reduction Capacity of Activated Carbon Fiber, *Carbon*, 2003, vol. 41, pp. 1265–1271.
7. Harry, I.D., Saha, B., and Cumming, I.W., Surface Properties of Electrochemically Oxidized Viscose Rayon Based Carbon Fibres, *Carbon*, 2007, vol. 45, pp. 766–774.
8. Ayranci, E. and Conway, B.E., Removal of Phenol, Phenoxide and Chlorophenols from Waste-Waters by Adsorption and Electrosorption at High-Area Carbon Felt Electrodes, *J. Electroanal. Chem.*, 2001, vol. 513, pp. 100–110.
9. Zemskova, L.A., Sheveleva, I.V., and Sergienko, V.I., RF Patent 2281160, 2006.
10. Scofield, J.H., Hartree–Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV, *J. Electron Spectrosc. Relat. Phenom.*, 1976, vol. 8, pp. 129–137.
11. Soffer, A. and Folman, M., The Electrical Double Layer of High Surface Porous Carbon Electrode, *J. Electroanal. Chem.*, 1972, vol. 38, pp. 25–43.
12. Veleshko, A.N., Rumyantseva, E.V., Veleshko, I.E., et al., X-Ray Photoelectron Spectroscopic Study of Uranyl–Chitosan Complexation, *Radiokhimiya*, 2008, vol. 50, no. 5, pp. 454–459.