Composition and Chemical State of Nanopowder Particles Obtained by Grinding Natural Diamond and by Detonation Synthesis

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Abstract. The initial composition and chemical state of primary particles of nanopowders obtained by grinding natural diamond and detonation synthesis have been investigated using X-ray photoelectron spectroscopy. It is shown that the primary particles of both nanopowders contain mainly carbon and oxygen atoms. Signals from nitrogen, sulfur, chlorine, and metal atoms do not exceed the noise level in the photoelectron spectrum. It has been found that in the primary particles of detonation synthesis nanopowder and nanopowder obtained by grinding natural diamond, the proportion of carbon atoms is ~ 46.5 and ~ 67.8% in the sp³-hybridization state, ~ 26.8 and ~ 17.4% in sp²– hybridization, and ~ 26.7 and ~ 14.7%, respectively, in the composition of oxygen-containing functional groups.

1. Introduction
Today, due to the combination of the unique physical and chemical properties of massive diamond and the dimensional effects inherent in nanoparticles, obtaining and investigating the properties of nanodiamonds are of particular interest to fundamental and applied science.

In the works [1, 2], nanodispersed powder of natural diamond (NND) was obtained by wet mechanical grinding, the specifics of the morphological characteristics and structural state of its primary particles were studied and analyzed. By the methods of transmission and scanning electron microscopy, X-ray diffraction phase analysis, small-angle X-ray scattering, and Raman spectroscopy it has been established that the NND nanopowder consists of particles with predominantly lamellar shape and a wider range of sizes, in contrast to detonation synthesis nanopowder (DND), which consists mainly of spherical particles of similar size. The atomic structure of primary particles obtained by grinding natural diamonds is similar to the structure of DND particles. That is, each particle of NND nanopowder, as well as DND particles, consists of a single-crystal diamond core surrounded by a shell with a complex structure containing mainly non-diamond forms of carbon with sp²-hybridization and impurities.

According to the generally accepted model, the primary particles of diamond nanopowders are supramolecules, in which a single-crystal diamond core, along with carbon atoms in sp³-hybridization, is surrounded by chemically bonded functional groups that are their integral part [3-6]. It has been established that the chemical composition and content of functional groups depend on the method and
conditions of the synthesis of nanodiamonds and their purification from non-diamond impurities [3-6]. In this regard, investigation of the composition and chemical state of the primary particles of nanopowder obtained by grinding natural diamond raw materials is of great interest.

The aim of the present work is the investigation and comparative analysis of the composition and chemical state of the initial (unmodified) particles of nanopowders obtained by grinding natural diamonds and detonation synthesis using X-ray photoelectron spectroscopy (XPS).

2. Objects and research methods

The XPS method, along with X-ray phase analysis and Raman spectroscopy, is the most informative method for studying the chemical and phase composition of nanoobjects that combines high sensitivity and spatial resolution. Line shifts and shapes in photoelectron spectra caused by the valence and chemical bonding of atoms ensure the use of XPS not only for determining the elemental composition but for studying the chemical bonds of nanostructured materials as well [5-7]. In our experiments, measurements were performed on a SPECS photoelectron spectrometer (Germany) using a PHOIBOS-150-MCD-9 hemispherical analyzer and a FOCUS-500 X-ray monochromator (AlK radiation, hν = 1486.74 eV, 200 W). The binding energy scale (Eb) was preliminarily calibrated according to the positions of the peaks of the core levels of Au4f7/2 (84.00 eV) and Cu2p3/2 (932.67 eV).

Several samples from one batch of natural diamond nanopowders with the average size of primary particles and specific surface area equal to ~ 24.0 nm and ~ 33.4 m²/g, respectively, were investigated. The method for obtaining nanopowder from natural diamond is described in detail in [1, 2].

To compare the chemical composition and state of primary particles of NND, samples of DND nanopowder of UDA-S-GO (manufactured by the Federal Research and Production Center Altai, Biysk) grade with an average size of primary particles of ~ 5.6 nm and a specific surface of ~ 338.6 m²/g were studied as well. According to the information received from the manufacturer, the given grade of nanopowder was subjected to additional deep purification using ion-exchange and membrane technologies after chemical purification from non-diamond impurities [8]. For the measurements, the samples of the studied nanopowders of NND and DND were applied onto a double-sided copper conductive tape 3M (USA).

3. Results

Figure 1 shows the survey photoelectron spectra of samples of DND (a) and NND (b) nanopowders that allow obtaining a general picture of the chemical composition of nanodiamonds and the presence of residual impurities or contaminants. The survey spectra were recorded at an analyzer transmission energy of 50 eV and individual spectral regions of 20 eV. As Figure 1 demonstrates, strong lines characteristic of carbon (C1s and C KVV) and oxygen (O1s and O KLL) appeared in the spectra of both DND and NND nanopowders. In addition to the indicated lines, weak peaks of nitrogen (N1s) and sulfur (S2s and S2p) (practically at the noise level) are observed in the DND nanopowder sample. According to the literature (for example, [3, 9]), DND particles usually contain appreciable amounts of nitrogen (from 2 to 8%) in addition to carbon and oxygen atoms. The low content of nitrogen in the presented DND samples (at the level of the background content) can be explained by the fact that the DND nanopowder of UDA-S-GO grade was subjected to additional deep purification using ion-exchange and membrane technologies after chemical purification. As a result, nitrogen atoms included in the composition of the sorbed molecules and functional groups were completely removed from the nanoparticles. In the sample of NND nanopowder particles, weak lines from metallic impurities: tungsten (W4f) and chlorine (Cl2p) were additionally recorded. No other chemical elements, which may be present in the form of impurities, were found in nanopowder particles within the sensitivity range of the XPS method.
Table 1 presents the results of measurements of the content ratio of the main elements - carbon and oxygen atoms, as well as the ratio of their atomic concentrations in the samples of DND and NND nanopowders. The relative content of elements on the surface of nanopowder samples and their atomic ratios were determined from the integral intensities of photoelectron lines corrected for the corresponding coefficients of atomic sensitivity [10]. As follows from Table 1, the ratio of the number of oxygen atoms to the number of carbon atoms for NND and DND nanopowder particles is approximately the same.

Table 1. Content ratio of carbon and oxygen in the samples of DND and NND particles and their atomic ratios.

| Nanopowder sample | C   | O   | C/O  |
|-------------------|-----|-----|------|
| DND               | 90.6| 9.4 | ~0.10|
| NND               | 90.8| 9.2 | ~0.10|

For a detailed analysis, the core lines of carbon C1s and oxygen O1s were decomposed into separate spectral components using the free XPSPeak 4.1 program [10]. Figure 2 shows the C1s and O1s lines in the photoelectron spectrum for (a) DND and (b) NND nanopowder samples.
Figure 2. Core lines of carbon C1s and oxygen O1s in the photoelectron spectrum for samples of DND (a) and NND (b) nanopowder.

As Figure 2 demonstrates, the contour of the C1s carbon line of the DND sample has a slightly asymmetric shape with a half-height width (FWHM) of ~ 3.07 eV and a relatively low intensity compared to the contour shape and the line strength of the NND sample, which has a half-height width of (FWHM) ~ 2.07 eV. According to the analysis of the binding energy values of individual components in the spectra of C1s lines of both DND and NND samples, the most intense peaks with binding energies of 285.3±0.2 eV correspond to sp³-hybridized carbon that forms a diamond crystal lattice [6, 9, 11-13]. The binding energy values of the peaks equal to 284.1±0.1 eV are characteristic of carbon atoms in the sp²-hybridization state (as in graphite or fullerenes) [6, 9, 11-13]. Peaks with binding energies of 286.6 eV correspond to carbon atoms in hydroxyl and ether groups (C-OH, C-O-C) [6, 9, 11-13]. The least intense peaks with binding energies of 287.9±0.3 eV characterize the state of carbon atoms in the composition of carbonyl and carboxyl groups (C = O, O = C-O, COOH). The presented data allows determining the amount of each state of carbon atoms to the total spectrum of the C1s line and the sp²/sp³ ratio for the measured samples of DND and NND nanopowders. These values are presented in Table 2. As follows from Table 2, approximately 46.5% of the total carbon atoms in the samples of DND nanopowder particles are in the state of sp³-hybridization, while ~ 26.8% of the atoms correspond to the state of carbon with sp²-hybridization. The rest of the carbon atoms are in the composition of hydroxyl (or ether) ~ 24.5% and carboxyl groups ~ 2.2% (Fig. 2 a). In
contrast to the primary DND particles, a significant part of carbon atoms (67.8% of their total amount) in the NND nanopowder samples is in the sp$^3$-hybridization state. The sp$^2$-hybridization carbon atoms amount to ~17.4%. The remaining ~13.0% of carbon atoms are contained in hydroxyl (or ether), and ~1.7% are in carboxyl groups (Fig. 2 b).

Table 2. Amount of carbon states in the total C1s spectrum (%) in DND and NND nanopowder samples.

| Nanopowder sample | sp$^2$, % | sp$^3$, % | C-O-C/COOH, % | COOH, % | sp$^2$/sp$^3$ |
|-------------------|----------|----------|----------------|--------|---------------|
| DND               | 26.8     | 46.5     | 24.5           | 2.2    | ~0.58         |
| NND               | 17.4     | 67.8     | 13.0           | 1.7    | ~0.26         |

The core lines of O1s oxygen in the DND (a) and NND (b) samples are demonstrated in Figure 2 on the left. The contours of the O1s oxygen lines of the DND (a) and NND (b) samples have almost the same intensity and shape with a half-height width (FWHM) of ~2.5 and 2.57 eV, respectively. It is seen that various oxygen-containing functional groups are present in the spectra of both samples. According to the literature data (for example, [9, 11-12]), oxygen peaks lie in the composition of carbonyl or carboxyl groups in the range of binding energies of 531.3–531.6 eV, while values of binding energies above 532.7 eV are characteristic of oxygen lines in the composition of hydroxyl and ester groups.

4. Conclusion

Thus, according to the results of the XPS study, the primary particles of NND nanopowders consist mainly of carbon (90.8%) and oxygen (9.2%) atoms, the remaining elements (N, W, Cl) appear at the level of trace amounts. DND particles have almost the same elemental composition as NND: 90.6% of carbon atoms, 9.4% of oxygen atoms, other elements including N and S atoms cannot be quantified, due to the weak signal intensity, which does not exceed the noise level. The low content of nitrogen in the DND particle samples can be explained by the additional deep purification of the initial UDA-S-GO nanopowder, as a result of which sorbed nitrogen molecules and nitrogen-containing compounds are removed from the nanoparticles.

In contrast to the primary particles of detonation synthesis, where the fraction of the total carbon atoms in sp$^3$-, sp$^2$–hybridization states and in the composition of the functional groups COC / C-OH, C = O and HO-C = O are ~46.5, ~26.8, and ~26.7%, respectively, the particles of nanopowder obtained by grinding natural diamond have the prevailing amount of carbon atoms in the state of sp$^3$-hybridization (~67.8%). The total fraction of carbon atoms in the sp$^2$-hybridization state does not exceed ~17.4%, and it reaches ~14.7% in the composition of oxygen-containing functional groups.

5. References

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