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Evaluation of the structural orientation of disordered sp^2 carbon using transmission microscopy and Raman spectroscopy

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The degree of structural orientation of natural disordered sp^2 carbon samples was studied using transmission electron microscopy and Raman spectroscopy. Using both methods, orientation was revealed in two samples, related to the external formation conditions. It was shown that even disordered carbon exhibits elements of structural anisotropy, which should be taken into account when analyzing and applying their physicochemical properties.

Keywords: natural disordered carbon, structure orientation, Raman spectroscopy, electron microscopy, image analysis.

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The degree of orientation of the structure, as well as the textural features of the microstructure, determine the spatial distribution of the physical and chemical properties of a substance and carry information about the conditions of its formation. If determining the crystallographic orientation for a crystal structure is a routine task of X-ray diffractometry [1,2], then in weakly ordered substances (in which there are no three-dimensional diffraction reflections, but there are reflections only from basal planes) the orientation of the structure is expressed implicitly, and its assessment is difficult due to the lack of long-range order. Nevertheless, a weakly expressed orientation (anisotropy) is often present in such objects It also significantly affects their physical and chemical properties. Unlike crystals, where their own crystalline texture plays a key role in the formation of orientation, in poorly ordered substances the presence and degree of orientation are more determined by external factors related to the conditions of formation. It is especially important to have an idea of the degree and direction of orientation of the structure in weakly ordered of sp^2 hybridized carbon substances such as carbon black, pyrocarbon, carbon metal, activated carbon, synthetic and natural glass carbon, since the mechanical, electrical, chemical properties of sp^2 carbon critically depend on the orientation graphene planes [3]. For example, the conductivity in the directions along and across these planes differs by several orders of magnitude.

High-resolution electron microscopy (HREM) [4,5] and Raman spectroscopy with different polarization [6–9] stand out among the methods for determining the presence and degree of orientation of the structure. HREM shows the relative location and orientation of atomic series directly (in the case of sp^2 carbon — graphene planes), which makes it the most effective method of high-resolution studies, however, this is achieved due to submicron locality, that is, small (within the image area of several hundred of nm^2 with a depth of up to one hundred nm) of the studied volume of the substance. In addition to orientation determination, Raman spectroscopy allows indirect evaluation of structural and textural features in a much larger volume (within the area of the laser beam, which is $5-30\,\mu m^2$ depending on the laser wavelength, with a penetration depth of several μm). The combination of these methods facilitates a detailed definition of the structure and an assessment of its orientation. The purpose of the study is to develop algorithms, create software, and define criteria for evaluating the orientation of the structure of disordered materials by mathematically analyzing HREM images and polarized Raman spectra using the example of naturally occurring disordered carbon substances.

To analyze the HREM images, an algorithm was developed that allows us to obtain the angular dependence of the concentration of horizontal lines of a digitized image filled with continuously arranged pixels. The procedure for analyzing HREM images is based on four algorithmic steps: (1) filtering of the digitized image in order to suppress noise in the image; (2) pixelation of bands corresponding to the atomic lattice of carbon; (3) sequential rotation of the image at angles up to 180°; (4) estimation of the total length of horizontal bands for each angle and compilation of the angular dependence of the total length of horizontal bands. The local maxima of this dependence correspond to the preferred orientation directions in certain areas of the image, and their angular width and the amount of excess over the

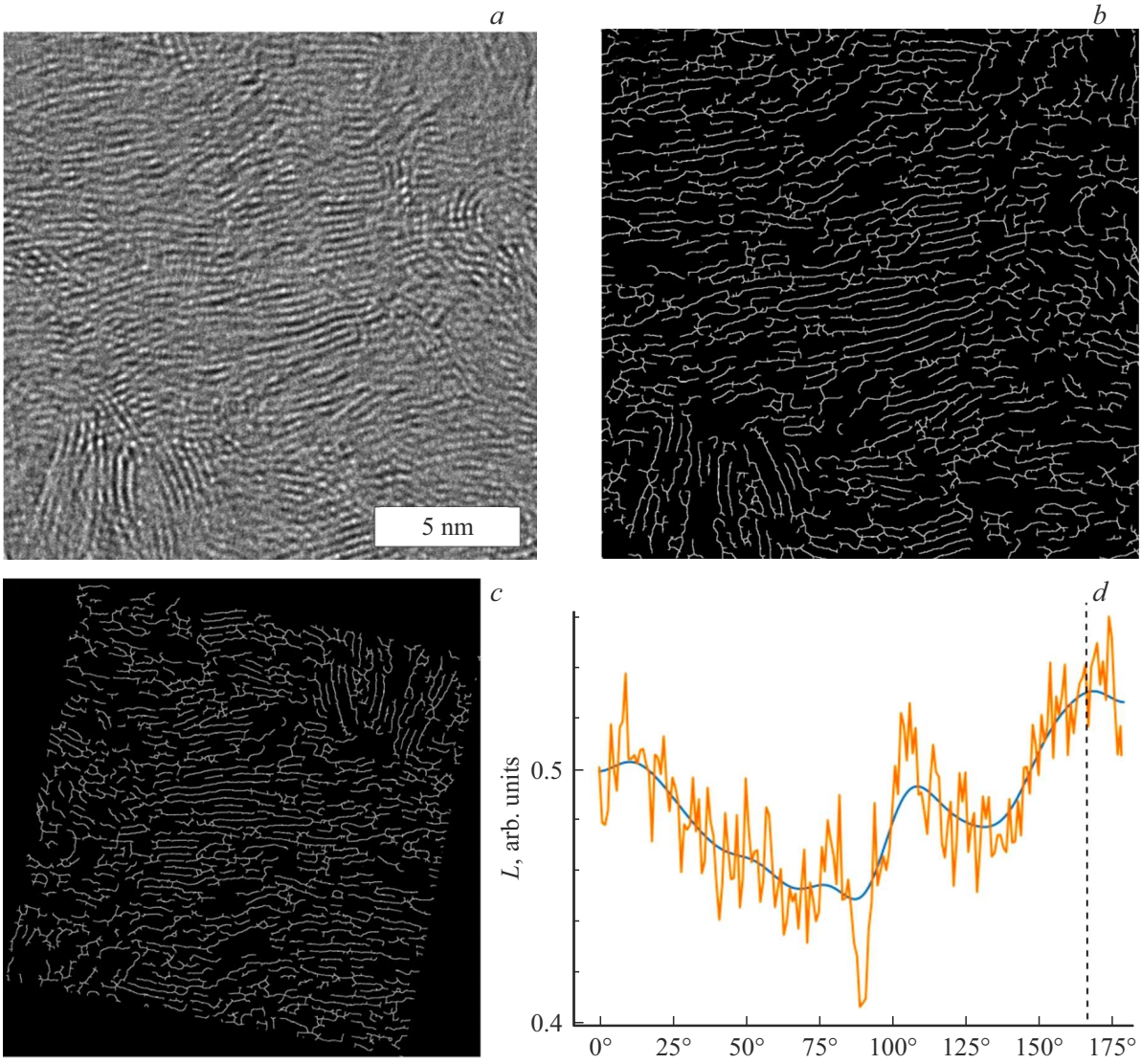

Figure 1. The main stages of determining the orientation of the structure from HREM images using the example of the ShSh1 sample: *a* — the original HREM image; *b* — filtered and skeletonized image („mask"); *c* — „mask", rotated by the angle of the prevailing orientation; *d* — angular dependence of the total length of the bands *L*.

background serve as evaluation criteria for the degree of orientation.

The algorithm was tested on four samples of naturally occurring disordered sp^2 carbon, structurally similar to synthetic glassy carbon [10]. The samples were taken from extended narrow cracks (Karelian shungites — ShSh1, Shunga deposit, and ShM1, Maksovo) and isotropic cavities (pores) with a diameter of several centimeters (shungite ShN1, Nigozero, and anthraxolite Columb, Columbia) in rocks. Cracks and pores in rocks are filled when liquid hydrocarbons of the petroleum series flow from the depths of the Earth's crust to the surface, while condensation and carbonation of hydrocarbons occur almost uniformly in the pores, and wall pressure is present in the cracks perpendicular to the direction of the hydrocarbon flow. Such differences in external conditions should affect the presence and degree of orientation of the carbon structure, even if it is poorly ordered.

Figure 1 shows an example of the result of the algorithm. Figure 1, *a* shows the typical structure of disordered sp^2 carbon, represented by bands — projections of planes of carbon atoms (graphene layers). These bands are grouped into stacks (domains) or into sinuous ribbon-like clusters, often enclosing pores. After filtering and skeletonization, a „mask" is created (see Figure 1, *b*), highlighting the structural component of the image. In this image, one main orientation direction of the structure is revealed (at 169° rotation) and two secondary ones (Figure 1, *c* and Figure 1, *d*). The secondary directions are associated with small mutually disoriented domains in the image, while the main direction characterizes the predominant orientation of the stripes.

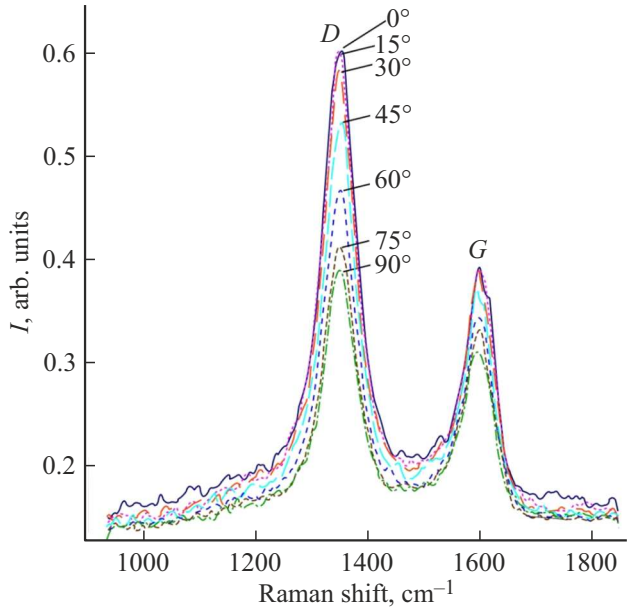

Figure 2. A typical single-phonon Raman spectrum (sample ShSh1) at different polarization angles (from 0 to 90°). There are two main bands of sp^2 carbon (G and D).

In general, three typical cases can be distinguished for the angular dependencies of the total length of horizontal bands. The first case with two or three narrow peaks, as in Figure 1, *d*, corresponds to the presence of several orientation directions associated with the presence of misdirected domains with comparable sizes. The second case is manifested by a single maximum of the total length of horizontal bands, the width of which depends on the degree of mutual orientation of the bands, and corresponds to the presence of a preferential orientation of the structure. The third case is associated with a misdirected structure in the sample, which is manifested by an almost uniform distribution of total length of horizontal bands in the corners. We will consider the first two cases as medium and high degrees of orientation, respectively.

Using the analysis of HREM images, a high degree of orientation was revealed for sample ShSh1, where the angular dependences exhibit a single broad peak with a half-width of 40–50°, clearly standing out above the background level. In the samples of ShM1 and ShN1, three or four orientation directions with a half-width of peaks are revealed in the images, as a rule, 25–30°. At the same time, if one predominant direction can always be distinguished in the ShM1 sample, then at least two directions in the ShN1 sample are always equivalent in intensity, which does not allow us to talk about the presence of a predominant orientation. The degree of orientation in these samples can be described as average. In Columb, the orientation of the structure is not determined, the angular distribution of the total length of horizontal bands is uniform.

The Raman spectra of carbon are represented by two main bands. The band G (about 1600 cm^{-1}) is associated with the fundamental mode $E_{2g}(2)$ [11], responsible for the vibrations of carbon atoms inside the graphene layer. The origin of the band D (approximately 1330 cm^{-1}) is still a matter of debate. For disordered carbon D, the band can be associated either with defects in the graphite structure [11], or with the manifestation of inhomogeneity in the length of the C=C bond in graphene domains due to the presence of heteroatoms and an increase in the number of graphene layers in the domains [12].

The polarized Raman spectra were measured by incrementally rotating the direction of polarization of the

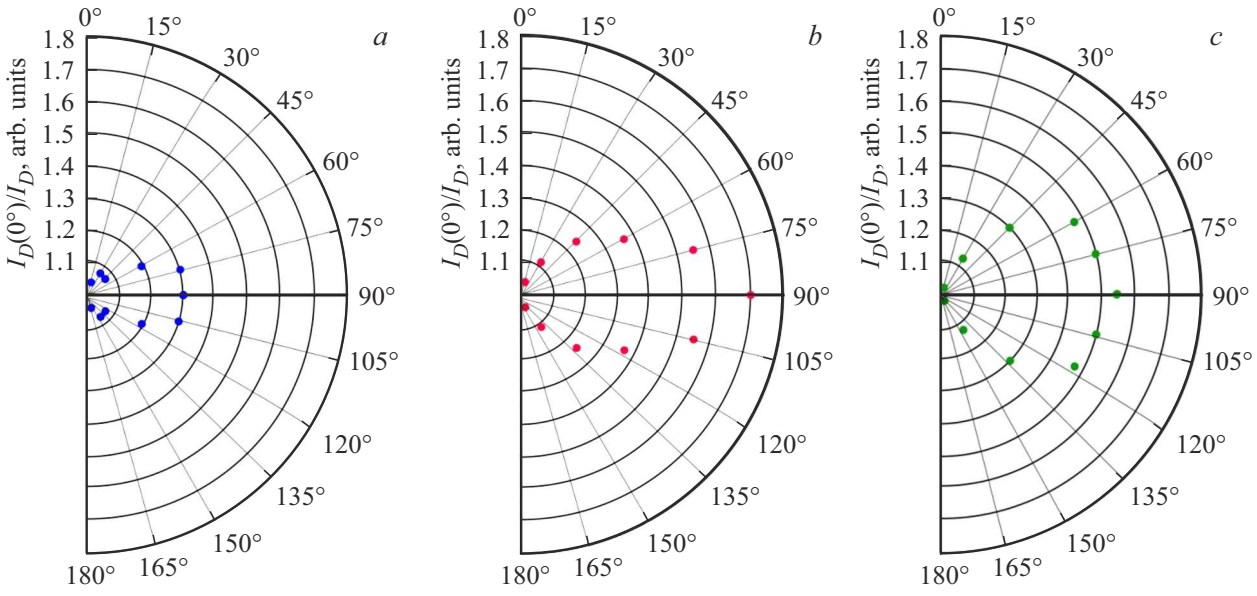

Figure 3. Polar graphs of the intensity of the Raman spectrum (based on the ratio of the intensity of the band D at different polarization angles to the maximum value at 0°). Samples: *a* — Columb; *b* — ShM1; *c* — ShSh1.

scattered radiation by 180° with a step of 15°. Figure 2 NT-MDT shows an example of spectra obtained in the range of polarization angles from 0 to 90°. A laser with a wavelength of 532 nm was used to excite the spectra. Polar dependences of the Raman intensity were obtained, the type of which is determined by the degree of orientation of the sample structure (Figure 3). Raman spectroscopy allows not only to determine the presence of orientation, but also to qualitatively assess its degree in relation to the intensity of the perpendicularly polarized bands $I_D(0°)/I_D(90°)$. A pronounced polarization dependence was recorded on samples ShSh1 (Figure 3, *b*) and ShM1 (Figure 3, *c*), where $I_D(0°)/I_D(90°)$ exceeds 1.5, and for samples Columb and ShN1 (the polar graph of which is close to the graph of the Columb sample, Figure 3, *a*) the intensity of the bands *G* and *D* weakly depends on the angle of polarization ($I_D(0°)/I_D(90°) \sim 1.3$), which indicates the misorientation of graphene domains in comparison with ShSh1 and ShM1.

The comparative results of the evaluation of the orientation of the structure by methods of HREM and Raman spectroscopy with different polarizations matched well for three samples: two samples with a high degree of orientation detected by both methods (ShSh1 and ShM1), and one sample (Columb) with a lack of orientation (low degree). These results correspond to the conditions of formation, since samples with a high degree of orientation were formed in cracks, where the orientation of the structure was expected to form along the direction of the crack, and the Columb sample was formed in the pores. The ShN1 sample, which was also formed in the pores, shows a low degree of orientation according to Raman spectroscopy and an average level of orientation according to HREM data. This difference in the results of the two methods for ShN1 is probably due to the high sensitivity of the REM study, which identifies local fragments of the oriented domain structure.

Thus, the work demonstrates the successful operation of an algorithm for estimating the presence and degree of orientation of a structure from HREM images, in combination with polarized Raman spectroscopy, using the example of samples of disordered natural sp^2 carbon. It is shown that the high sensitivity of the algorithm to small areas of the structure with pronounced orientation (domains) does not prevent the identification of the predominant orientation direction against their background, and also demonstrates the good capabilities of polarized Raman spectroscopy in determining the textural parameters of the disordered structure of sp^2 carbon.

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Conflict of interest

The authors declare that there is no conflict of interest.

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