Effect of high pressures and temperatures on carbon nano-onion structures: comparison with C_{60}

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The results of investigations of the structure and properties of carbon nano-onions before and after high-pressure high-temperature (HPHT) treatment are presented. The onion structures are retained after HPHT treatment up to 15 GPa and 1450 °C, which was confirmed by X-ray diffraction, electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The HPHT treatment was shown to increase the hardness and the density of these carbon forms due to the formation of sp^3-hybridized carbon atoms.

Key words: carbon, onion structures, graphene layers, fullerite C_{60}, X-ray diffraction, electron microscopy, X-ray photoelectron spectroscopy, high pressures, high temperatures.

Earlier,[1—4] new polymeric carbon materials, including materials having the diamond- and higher-level hardness, have been synthesized from fullerites C_{60} and C_{70} by the high-pressure high-temperature (HPHT) technique. Since the properties of these materials depend substantially on the composition and the structures of the starting carbon substances, it was of interest to use onion-like carbon structures (onions) as precursors for new carbon materials using the HPHT technique.

These onions are multilayer nanostructured particles composed of graphene layers curved into closed-shell structures resembling multilayer fullerenes.[5] Onion structures have attracted interest after the development[6] of a reproducible method for the preparation of these structures by intense electron-beam irradiation of carbon soot.

There are several experimental methods for the preparation of onions. However, in terms of the practical use, one of the most efficient methods is based on the heating of nanodiamonds *in vacuo* or in gaseous media at nearly atmospheric pressure.[7] This method was used in the present study.

Since this discovery and up to the present time, the properties of onions have been studied only for powdered materials, which hampered their use in high-tech devices, for example, in electronics.[8] The methodological problem in the compaction of onions is that high pressures and high temperatures are required for the production of bulk materials from onions.

The aims of the present study were to elucidate whether it is possible to produce superhard materials from onions, as it was shown for fullerite C_{60}, and to investigate the properties of the materials prepared from onions by the HPHT technique.

Experimental

High-pressure phases were prepared and kept under ambient conditions with the use of an improved "anvil with a hole," which produces high pressures up to 15 GPa.[9] High pressures were generated in a chamber consisting of two coaxial profiled hard alloy (tungsten carbide cobalt) anvils pressed into steel rings, between which a container containing a heater and a sample is sandwiched. The chamber was placed in a hydraulic press generating the load up to 2500 tons. The pressure was measured at room temperature based on the jumps in electrical resistance in reference metals and compounds: Bi (7.7 GPa), Sn (9.5 GPa), Ba (12.5 GPa), Pb (13 GPa), ZnSe (13.7 GPa), and ZnS (15 GPa).

Samples were heated by resistive graphite heaters. The temperature was measured with chromel—alumel and Pt—PtRh thermocouples. To prevent contamination, the samples were wrapped in a tantalum foil.

The experiments were carried out at a pressure of 7.7, 9, and 15 GPa in the temperature range of 500—1500 °C. The samples

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were kept under isothermal conditions for 1 min and then quenched in the following way: after the termination of the heating, the chamber was cooled at a rate of 50 °C s^{-1} and then the pressure was released at a rate of 0.5—1 GPa min^{-1}.

Nano-onions were prepared according to a procedure described earlier.[7] Detonation nanodiamonds were heated in a vacuum chamber ($5 \cdot 10^{-3}$ Torr) at 1600 °C, the target temperature was reached during 60 min, and then the samples were kept at 1600 °C for 30 min.

After the removal from the high-pressure chamber, the samples were analyzed at atmospheric pressure and room temperature by X-ray powder diffraction, HREM (high-resolution electron microscopy), XPS (X-ray photoelectron spectroscopy), and Raman spectroscopy. The X-ray powder diffraction patterns were measured on an ARL X´TRA powder diffractometer (Cu-Kα radiation) equipped with a solid-state (Si(Li)) semiconductor detector.

The HREM experiments were carried out on a JEM-2010 instrument; the accelerating voltage was 200 kV.

The Raman spectra were measured on an RFS100/S Fourier-transform Raman spectrometer at 4 cm^{-1} resolution using excitation with the Nd laser line at λ = 1064 nm.

The photoelectron spectra were recorded on a PHI 5500 ESCA instrument using Mg-Kα radiation ($h\nu$ = 1253.6 eV); the power was 300 W). The high-resolution C1s photoelectron spectra were obtained over a narrow energy range (270—296 eV) with an analyzer pass energy of 11.75 eV and the data collection rate of 0.1 eV $step^{-1}$; the spectra over a broad energy range (270—350 eV), including the C1s peak and its satellite, were collected with 93.9 eV and 0.8 eV $step^{-1}$, respectively. The residual gas pressure in the analysis chamber was at most $7 \cdot 10^{-8}$ Pa.

All methods confirmed that carbon onions with a size in the range from 5 to 20 nm were produced from nanodiamonds. Samples of onions were identified by HREM, Raman spectroscopy, and XPS as carbon materials with curved graphene planes.

The mechanical properties of the starting powdered onions are similar to those of graphite-like structures. The microhardness of the samples was evaluated with a PMT-3 microhardness tester by impressing a Vickers diamond indenter into a prepolished sample.

The densities of the samples were determined by flotation in diiodomethane—acetone mixtures at different concentrations, which allowed the measurement of small particles with a weight of 1 mg (the accuracy of the determination of the density was ±0.03 g cm^{-3}).

Results and Discussion

X-ray diffraction and electron microscopy studies. The starting detonation diamond was a powder with a particle size of <5 nm. Most of the onions (Fig. 1) have a polyhedral structure; the size of some particles is larger than the size of the starting nanodiamond particles.

It is known that spherical onions are transformed into polygonal structures at annealing temperatures higher than 1900 °C.[10—12] In our experiments, the annealing temperature was not higher than 1600 °C, but the amount of polygonal onions was substantial. Most likely, this is attributed to the fact that we used longer annealing time (30 min) compared to the times used in the earlier studies[9—12] (for example, 5—10 min in the study[12]).

Fig. 1. HREM image of the starting sample of an onion (**1**).

The diffraction patterns of onions after the high-pressure (7.7 GPa) and high-temperature (500—1350 °C) treatment are displayed in Fig. 2. The diffraction pattern *1* was obtained from the starting nanodiamond powder. In the diffraction patterns of the onions, no diamond peaks were observed.

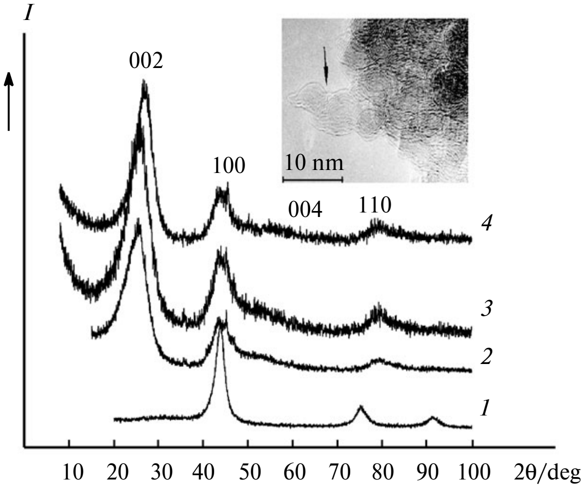

Fig. 2. Diffraction patterns of the starting nanodiamonds (*1*) and onions **1** (*2*) and samples of onions **3** and **4** after the treatment at a pressure of 7.7 GPa at 500 (*3*) and 1350 °C (*4*), respectively. The numbers above the peaks are the Miller indices in the graphite-type structure. The inset shows the HREM image of the structure of sample **4**; a row of adhered onions is indicated by an arrow.

As can be seen from Fig. 2, the reflection 002 is shifted to larger 2θ angles with increasing temperature of the treatment. Thus for sample **3**, the interplanar spacing d_{002} = = 3.33 Å, whereas d_{002} = 3.54 Å for the starting onion sample (**1**).

The distances between the outer and inner shells of the onions after HPHT treatment, which were estimated from the HREM images, became equal. Thus, the pressure facilitates the tighter arrangement of the shells of the onion-like structure and does not destroy the structure. Apparently, a certain number of adhered onions linked by bridges composed of sp^3-hybridized carbon atoms is formed. The HREM image presented in the inset to Fig. 2 indirectly confirms this hypothesis; a row of adhered onions is indicated by an arrow.

The diffraction patterns of the onions produced by the high-pressure treatment (15 GPa) in the same temperature range are presented in Fig. 3. The inset *a* to Fig. 3 clearly shows that onions are tightly bound together and often intertwine.

The diffraction pattern and the HREM image for fullerite C_{60} after the the treatment at 9 GPa and 1000 °C are shown for comparison. The diffraction pattern and the HREM image of fullerite C_{60} have much in common with those of the onions. Thus, the structures of both substances consist of deformed spherical or ellipsoidal shells. In other words, the spheroidal structure of C_{60} is destroyed upon HPHT treatment. Hence, hereinafter we will refer to this substance as «C_{60}».

Like the diffraction patterns of the samples obtained under lower pressure (see Fig. 2), the diffraction patterns presented in Fig. 3 show reflections (002, 100, 004, and 110), which are indicative of the absence of the three-dimensional periodicity in the structures of the onions. The diffraction pattern of «C_{60}» also has only these reflections. In all diffraction patterns (see Figs 2 and 3), the reflection 002 is strongly asymmetric and broadened, which is characteristic of the diffraction patterns of onions.[13] Due to this distinguishing feature, we chose carbon onions as potential precursors for the construction of superhard materials because we have earlier found a solid phase of fullerite C_{60} produced at 9 GPa and 1000 °C, which is characterized by the similar diffraction pattern and has a disordered layered structure.[14] In all diffraction patterns (see Figs 2 and 3), the *hkl* reflections corresponding to atoms in general positions are absent, *i.e.*, the structures of all samples before and after HPHT treatment remain turbostratic.

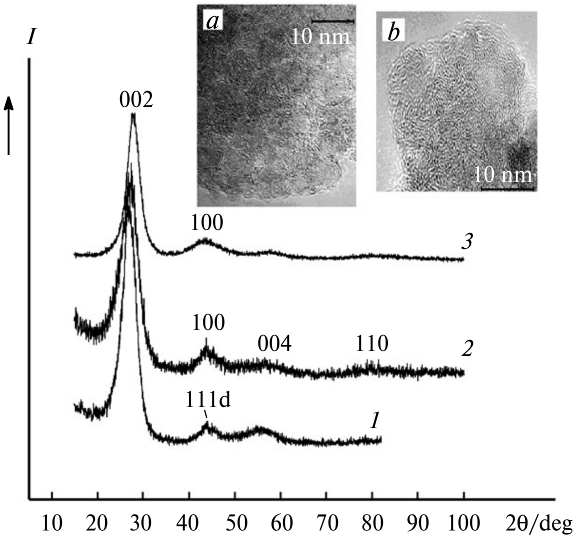

Fig. 3. Diffraction patterns of onions (*1*, *2*) and fullerite C_{60} (*3*) after HPHT treatment: T = 1400 °C, P = 13 (*1*) and 15 GPa (*2*), T = 1000 °C, P = 9 GPa (*3*). The insets *a*, *b* show the HREM images of the structures of the latter two samples. The reflection 111d in the diffraction pattern *1* is the diamond reflection.

The interplanar spacings d_{002} in the structures of onions and «C_{60}» are given in Table 1. An increase in the pressure and temperature has a substantial effect on the close arrangement of graphene shells in onions. Thus the HPHT treatment (P = 7.7 GPa, T = 500 °C) of the starting onion samples leads to a decrease in the inteplaner spacing d_{002} from 3.54 to 3.46 Å; at P = 15 GPa and 500 °C, d_{002} decreases to 3.39 Å. An increase in the tem-

Table 1. Interplanar spacings d_{002}, the densities ρ, and the hardnesses HV of samples of onions and fullerite «C_{60}» obtained at high pressures (P) and temperatures (T), and the K values for the X-ray photoelectron spectra

Sample	P/GPa	T/°C	d_{002}/Å	ρ/g cm^{-3}	HV/GPa	$K = S_{AB}/S_{AC}$	K/K_0*
1	1 atm.	25	3.54	—	—	2.78	1.00
2	7.7	500	3.46	2.05	2.5	2.72	0.98
3	7.7	1350	3.32	2.07	5.7	2.34	0.84
Onion (**4**)	15.0	500	3.39	—	—	—	—
Onion (**5**)	15.0	1400	3.28	2.16	12.0	2.31	0.83
«C_{60}» (**6**)	9.0	1000	3.20	2.25	30—40	—	—
«C_{60}» (**7**)	13.0	1400	—	3.29	170.0	—	—

* K_0 is the value for the sample of the starting onion (**1**).

perature leads to a decrease in d_{002} by ~0.1—0.15 Å. For example, at 15 GPa and 500 °C, d_{002} = 3.39 Å; at 1400 °C and the same pressure, d_{002} = 3.28 Å (see Table 1).

The main difference between the diffraction pattern of «C_{60}» (see Fig. 3 and Table 1, sample **6**) and the diffraction patterns of onions is a more substantial decrease in the reflection 002. Thus d = 3.20 Å for «C_{60}», whereas onions (see Fig. 3, curve *2*; Table 1, sample **5**) are characterized by d = 3.28 Å, but the P and T parameters of treatment of onions were much stronger than those of fullerite C_{60}. The reflection 004, which is the second order of the reflection 002, is very weak in the diffraction patterns of onions, but it also decreases. In all diffraction patterns (see Figs 2 and 3), the reflections characterizing graphene planes (reflections 100 and 110) are almost not shifted, but they are substantially broadened and become asymmetric, which is indicative of the presence of defects and violation of the periodicity in the graphene shell.

A decrease in the interlayer distance after HPHT treatment has a considerable effect on the elastic properties, for example, on the hardness and the density. An increase in the hardness and density with decreasing d_{002} is characteristic of all the samples under study. Table 1 gives also data for superhard fullerite (sample **7**) produced at 13 GPa and 1400 °C,[15] which also has a spheroidal structure composed of graphene shells.[16] The hardness of this sample determined by nanosclerometry is equal or even higher than that of diamond (170 GPa).[15]

A comparison of the onions with C_{60} (see Fig. 3, insets *a* and *b*) shows that the spheroidal structure of «C_{60}» is more distorted and contains almost no completely closed shells. The diffraction pattern of «C_{60}» (see Fig. 3, curve *3*) has more symmetric and more intense peaks compared to those observed in the diffraction patterns of the onions. Hence, the structure of «C_{60}» belongs to layer-type structures. Based on the X-ray diffraction and HREM results, it can be suggested that this modification of «C_{60}» does not contain fullerene molecules, their cages are destroyed during HPHT treatment, but curved graphene shells still consist of layers composed of carbon atoms forming hexagons and pentagons. The HPHT treatment results in that these layers are brought into close proximity and are pressed together to form a tight structure. After HPHT treatment, the structure of onions also resembles layered structures, but the onions are not destroyed, which accounts for the larger interlayer distance in their shells compared to «C_{60}».

Raman and XPS studies. Onions were studied by Raman spectroscopy and XPS with the aim of determining the character of bonds between carbon atoms.

The Raman spectra of onions **4** and **5** (see Table 1) are displayed in Fig. 4. The bands at 1350 and 1590 cm^{-1} in the Raman spectrum of onion **4** are characteristic of polycrystalline graphite. The Raman spectrum of onion **5** shows, in addition to graphite bands, a shoulder at 1430 cm^{-1}, *i.e.*, in the region of vibrations of pentagons in fullerene structures. For sample **5**, the smallest spacing is d_{002} (3.28 Å, see Table 1); sample **4** was taken for comparison. It was hypothesized that the shortened distance is due to the presence of sp^3-hybridized carbon atoms responsible for strong elastic properties. Unfortunately, due to the low Raman cross-section of sp^3 bonds upon Nd laser excitation, their contribution to the resulting spectra was negligible. The Raman spectra of sample **4** correspond to the spectra of disordered polycrystalline graphite, whereas the spectrum of onion **5** shows high-frequency shifts of both stretching vibrations of the carbon atoms (G mode) to 1592 cm^{-1} and "defect" vibrations of the carbon atoms to 1364 cm^{-1}. Most likely, these shifts reflect a decrease in the interatomic C—C distance. The frequency of this band is similar to the frequency of the maximum, which has been found earlier[17] in the Raman spectra and assigned (like those in the Raman spectra of «C_{60}») to tangential motions of the carbon atoms in pentagons in the shell structure of onions.

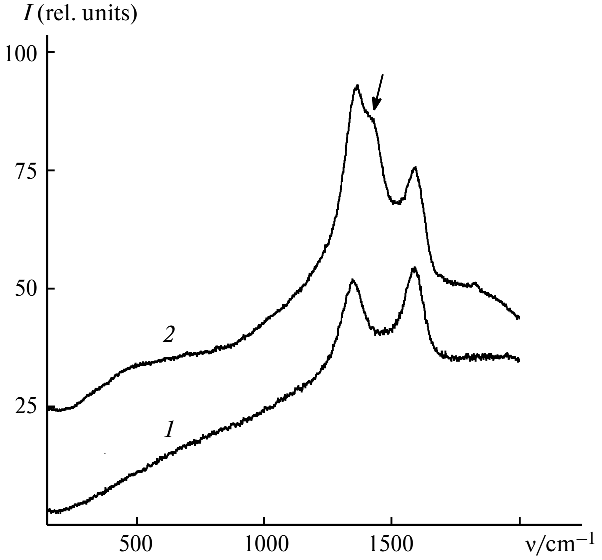

Fig. 4. Raman spectra of samples of onions **4** (*1*) and **5** (*2*).

The XPS spectra include two regions: the main C1s peak (Fig. 5, *AB* region) and the related σ-plasmon satellite[18] (Fig. 5, *AC* region). The satellite *AC* is associated with losses due to the excitation of valence electron plasmons, and its relative intensity is higher for sp^3-hybridized atoms. The spectra of the C1s peak and the satellite (see Fig. 5) provide qualitative data on a decrease in the percentage of sp^2-bound carbon atoms (the narrowing of the spectrum in the *AB* region) and an increase in the percentage of sp^3-hybridized carbon atoms (the broadening of the spectrum in the *AC* region) with an increase in the temperature and pressure of the sample treatment.

The quantitative results are given in Table 1. The percentage of sp^3 bonding was quantitatively evaluated based

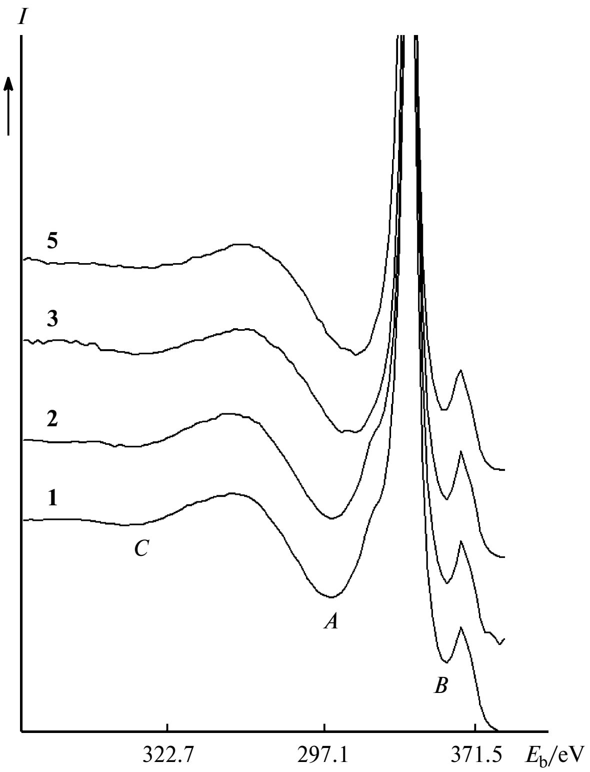

Fig. 5. Spectra of the C1s peak and its σ-plasmon satellite of onions **1**—**3** and **5**.

on the coefficient K, which is equal to the ratio of the surface area of the spectrum in the AB region to the surface area of the spectrum in the AC region. For graphite, $K = 2.5$ and it corresponds to 100% sp^2 bonding; for fullerene C_{60} and single-layer nanotubes composed of curved graphene planes, the coefficient K is higher than that for graphite (for the face-centered cubic lattice of C_{60} and single-layer nanotubes, $K = 3.1$). For samples of onions **1** and **2**, $K = 2.78$ and 2.72, respectively (see Table 1), which corresponds to the carbon forms with curved graphene planes. For samples **3** and **5** (see Table 1), the coefficient K is smaller, which is indicative of the presence of sp^3 bonds, because the value of K for diamond (100% of sp^3 bonds) is 1.55.

The formation of sp^3 bonds in samples of onions **3** and **5** (see Table 1) is also evident from the analysis of the high-resolution C1s photoelectron spectra (Fig. 6). The spectral shape for sample **2** is characteristic of the predominant sp^2 bonding. Thus the spectrum is characterized by the asymmetry and the presence of the π—π* satellite in the region of 290—291 eV; its percentage is 12%. Figure 6 shows changes in the C1s photoelectron spectrum with increasing pressure and temperature of the treatment. The asymmetry of the C1s photoelectron spectrum of sample **3** is substantially smaller, the intensity of the π—π* satellite substantially decreases, and the percentage of the latter is at most 5%. For sample **5**, the asymmetry the C1s photoelectron spectrum and the π—π* satellite virtually disappear. The relative content of sp^3-hybridized carbon atoms, which was estimated from the relative fraction of the peak *2* in the common spectrum of sample **5**, is 15—20%.

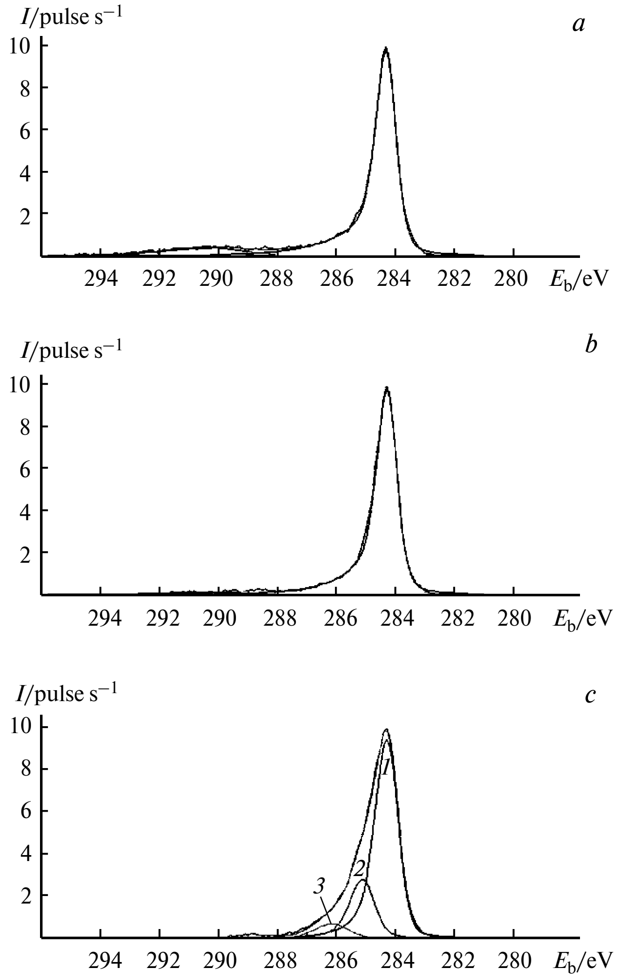

Fig. 6. Spectra of the C1s peak of onions **2** (*a*), **3** (*b*), and **5** (*c*).

In conclusion let us mention that the results of the present study show that onions as a whole and their graphene layers are highly stable. The size of the onions remains unchanged (~5 nm) even after the treatment at the maximum pressure (15 GPa) and temperature (1400 °C) (see Fig. 3, inset *a*). Apparently, the spheroidal multilayer structure of graphene layers in onions is responsible for the fact that the interlayer distance cannot be decreased to such considerable values that are observed in destroyed single-layer fullerene molecules.

Presumably, an increase in the hardness of onion-like samples with an increase in the HPHT parameters is associated with the reverse process producing a certain amount of diamonds from onions, as has been noted in a number of studies.[19,20] We also observed the appearance of the very weak reflection 111 corresponding to diamond in one diffraction pattern (see Fig. 3, curve *1*). The very low relative intensity of the latter reflection did not allow us to determine other reflections of diamond, evaluate the amount of diamond in the resulting substance, and estimate its influence on the hardness of the samples.

To sum up, the HPHT treatment of onions does not lead to the production of superhard materials; however, onions have high hardness and stability, which are in some cases sufficient for the practical use. In addition, our preliminary investigations showed that bulk compact samples produced by HPHT treatment of powdered onions are characterized by electrophysical, including autoemission, properties.

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