

Thermally Stable Hydrogen Compounds Obtained Under High Pressure on the Basis of Carbon Nanotubes and Nanofibers

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Received February 3, 2004

Compounds containing 6.3–6.5 wt % H and thermally stable in vacuum up to 500°C were obtained by annealing graphite nanofibers and single-walled carbon nanotubes in hydrogen atmosphere under a pressure of 9 GPa at temperatures up to 450°C. A change in the X-ray diffraction patterns indicates that the crystal lattice of graphite nanofibers swells out upon hydrogenation and that the structure is recovered after the removal of hydrogen. It was established by IR spectroscopy that hydrogenation enhances light transmission by nanomaterials in the energy range studied (400–5000 cm⁻¹) and results in an appearance of absorption bands at 2860–2920 cm

The interaction of carbon nanostructural materials with gaseous hydrogen has been intensively studied over the last five years. The developed surface of these materials causes considerable applied interest that is aimed at producing hydrogen accumulators and reducing the consumption of organic fuel in modern industry. For the academical studies, of interest is the character of hydrogen interaction with carbon nanotubes and nanofibers. In the published works, the saturation of nanostructures with hydrogen was carried out under relatively mild conditions; the hydrogen pressure did not exceed 100–120 atm (10–12 MPa) at liquid nitrogen or room temperature (see, e.g., review [1]). The data of different authors on the maximal amount of accumulated hydrogen show a scatter of two orders of magnitude, from several tenths to several tens of H wt %. As the general regularity, the processes of hydrogen absorption and release in the cycles of pressure buildup and reduction were found to be reproducible at both room and nitrogen temperatures. Based on the data on the hydrogen absorption and release as functions of pressure or temperature, most authors assume that physisorption of H₂ molecules on the graphene layers is the dominating mechanism of hydrogen absorption. The studies of physical properties are few in number. The results of recent measurements of electronic transport properties and Raman spectra of single-walled nanotubes during the course of hydrogen adsorption and

desorption at pressures up to 8 atm and temperatures from 4 to 500 K [2] are in accordance with the assumption about hydrogen physisorption. The maximal hydrogen content in nanotubes subjected to deep purification exceeded 6 wt % at pressures from 2 to 20 atm and a temperature of 77 K [2].

The chemical potential of hydrogen increases under pressure, and there are many examples of the increase in hydrogen solubility or the formation of hydride phases in the metal–hydrogen systems at high pressures. In this work, the interaction of hydrogen with carbon nanostructures—graphite nanofibers (GNF) and single-walled carbon nanotubes (SNT)—is studied upon the thermal treatment with maximal parameters of 9 GPa and 450°C. The treatment gave the samples that contained up to 7 wt % H and differed from the nanostructures hydrogenated under mild conditions by a higher thermal stability: the main hydrogen mass was released at $T \geq 500^\circ\text{C}$.

Starting GNFs were synthesized in a direct-flow quartz reactor in a CO : H₂ = 4 : 1 gas mixture at 600°C for 6 h using a mixed Fe : Cu = 7 : 3 catalyst. Scanning electron microscopy showed that the GNF length was, on the average, 30 μm and the diameter ranged from 100 to 300 nm. The content of graphite nanofiber in the prepared material was about 90%.

Carbon black containing 15–20% SNT was synthesized by the electric arc method in helium atmosphere at a pressure of 0.86 atm using a metallic Co : Ni = 3 : 1 catalyst [3]. To remove impurities from SNT, carbon black was subjected to ultrasonic treatment in a concentrated hydrochloric acid, whereupon to the multistage treatment with hydrochloric acid alternating with oxidation in air at temperatures up to 540°C. The content of single-walled nanotubes in the product was estimated using scanning and transmission electron microscopies and was found to be equal to 50–60%.

In the experiments, a GNF or SNT sample with a mass of about 60 mg was placed in a high-pressure chamber and saturated with hydrogen obtained by thermal decomposition of AlH_3 . The sample was held under a hydrogen pressure of 9 GPa first for 18 h at $T = 350^\circ\text{C}$ and then for another 6 h at 450°C . At the end of holding, the chamber was cooled to -140°C and unloaded to atmospheric pressure at this temperature. Then the

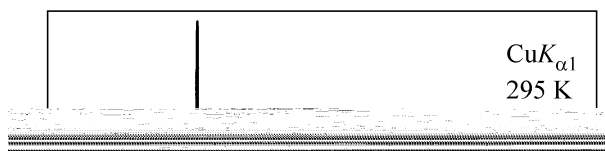


Fig. 2. X-ray diffraction patterns of single-walled carbon nanotubes and graphite nanofibers: in the initial state, after saturation with hydrogen at 9 GPa (6.8 and 6.3 wt % H, respectively), after removal of about 40% of absorbed hydrogen (4.3 and 3.6 wt % H), after degassing annealing to 600–650°C (1.7 and 1.2 wt % H), and after prolonged annealing at 700°C (GNF). For comparison, the diffraction pattern of a GDG-6 graphite powder is also shown. Bar diagrams of Fe and Cu indicate the catalyst admixture in GNF. Room temperature.

to be drawn that, after measurements with heating to 600–650°C presented in Fig. 1, about 1.2 and 1.7 wt % H remained in the GNF and SNT samples, respectively.

Figure 2 shows the X-ray diffraction patterns of GNFs and SNTs in the initial and hydrogenated states and after various annealing procedures. Partial annealing with the removal of ~40% of hydrogen absorbed under pressure (the residual contents were 3.6 wt % H in GNF and 4.3 wt % H in SNT) was carried out with holding the sample in an evacuated volume at a temperature of about 500°C, until the pressure of released gas reached the calculated value. Annealing of GNF at 700°C was performed in a dynamic vacuum of $<10^{-5}$ mmHg for 6 h. The X-ray diffraction pattern of the ground high-density graphite GDG-6 is presented in Fig. 2 for the comparison. Measurements were made at

room temperature on a D500 Siemens diffractometer with the monochromatized $\text{CuK}_{\alpha 1}$ radiation.

The diffraction patterns of initial GNFs include a strong reflection near the graphite (002) line at $2\Theta = 26.5^\circ$, a number of weak reflections near the other graphite lines, and the lines of catalyst components. After the saturation of GNF with hydrogen, a broad intense peak appears near 19° instead of a very strong graphite reflection, while the other graphite reflections undergo a marked shift to small angles, and only the catalyst lines do not change their positions. After two heating cycles to 600°C shown in Fig. 1, the peak at 19° disappears and the diffraction pattern mainly regains its initial shape. Nevertheless, the most intense reflection remains markedly shifted to small angles, in agreement with the fact that hydrogen is removed incompletely. A prolonged vacuum annealing at 700°C results in a complete recovery of the initial diffraction pattern. A comparison of the diffraction pattern of the sample having 3.6 wt % H after partial annealing with the diffraction patterns of the extreme states shows that it represents the diffraction pattern of a two-phase state, in which the strongest reflections are shifted toward each other ($2\Theta \approx 19.9$ and 24.0°) and are strongly broadened.

In the diffraction pattern of the initial SNTs, no reflections are seen from the nanotubes (a weak reflection can be, in principle, observed at small angles ($2\Theta \sim 6^\circ$) because of the triangular SNT packing in beams; see, e.g., [15]). A sharp weak reflection at the position of the graphite (002) line should be caused by the presence of an admixture of graphitized particles in the material. The catalyst reflections are not seen. After the hydrogenation of SNT, a broad peak appears near 18.5° , while the narrow graphite (002) and (004) reflections are markedly strengthened. The removal of 2.5 wt % H results in weakening of the broad peak and its shifting by $\sim 0.8^\circ$ to larger angles, and this peak disappears after heating to 650°C. The sharp graphite (002) and (004) reflections are retained and their intensity relative to the background changes only slightly. It was reported in the literature that SNT is not destroyed at hydrostatic pressures below 13 GPa [5]. For this reason, a change in the diffraction pattern of SNT after the thermal treatment in hydrogen should be assigned to the graphitization of amorphous carbon particles in the initial material and to the hydrogenation and dehydrogenation of a certain fraction of graphitized particles.

Weakly bonded hydrogen, which is released in an amount of less than 0.5 wt % upon heating to room temperature, can reasonably be assigned to physisorption, which is considered to be the dominant mechanism of hydrogen absorption by carbon materials at pressures below 12 MPa and not too high temperatures. To elucidate the nature of the bonded state of the main hydrogen mass that is retained up to high temperatures, the IR diffuse reflection spectra were measured for GNF and SNT in the initial state, after the treatment under hydrogen pressure, and after the degassing annealing. Mea-

measurements were performed in the range 400–5000 cm^{-1} at room temperature on a Bruker IFS-113v IR Fourier spectrometer. The results are presented in Fig. 3.

The diffuse reflection carries information, primarily, about the transmission spectrum of the sample [6]. The spectra of initial GNFs are characterized by a monotonic decrease in transmission with increasing photon energy; such a spectral behavior is typical of the spectra of purified nanotubes [7]. As in the case of nanotubes exhibiting properties of a strongly imperfect metal or semimetal, the light absorption by free charge carriers caused by their high-frequency conductivity is the most probable reason of a decrease in the GNF transmission with increasing photon energy. In the spectra of initial SNTs, a broad transmission minimum near 2600 cm^{-1} is superposed on the free-carrier absorption. The anomalies of this type were observed earlier and discussed in detail for granulated composite materials consisting of the conducting and nonconducting components (see [8] and references therein).

After the hydrogenation, the GNF transmission increases substantially over the entire range of measurements, and a narrow absorption band at 2860 cm^{-1} with a halfwidth of 38 cm^{-1} and a weaker band at 2920 cm^{-1}

mately 40% from 3.36 to 4.67 Å. The increase in c as large as that allows one to assume that the third state is a molecular hydrogen situated between the graphene layers in the nanofiber bulk. This assumption explains the two-phase diffraction pattern of the partially annealed GNF sample containing 3.6 wt % H, which, likely, is characterized by the presence of concentrational inhomogeneity and microstrains. The idea of accumulation of molecular hydrogen between the graphene layers was put forward earlier when studying the interaction of atomic hydrogen with graphite [9] or in the study of the interaction of hydrogen with graphite during the grinding process in ball mills [10, 11]. However, the diffraction measurements in these works were hampered by the fact that the penetrability of atomic hydrogen was limited by only one carbon layer [9], while the grinding in a mill rapidly brought the sample into the amorphous state [10, 11].

The question of the hydrogen positions in the hydrogenated SNT product at normal conditions is more complicated. The possibility of hydrogen molecule penetrating through the wall of a closed SNT was theoretically considered in [12]. However, one should take into account that our product contains from 40 to 50 wt % of impurity carbon nanoparticles that crystallize upon thermal treatment and take part in the hydrogenation and dehydrogenation processes. All structure reflections in the SNT diffraction patterns are, likely, caused by the presence of such (multilayer) particles in the hydrogenated or nonhydrogenated states. The hydrogen absorption by the SNT product (6.8 wt % H, as compared to 6.3 wt % H in GNF), nevertheless, cannot be explained by the hydrogenation of impurity carbon particles alone, because they comprise the smaller part of the sample and are hydrogenated incompletely. It is reasonable to assume that the amounts of hydrogen in the carbon nanoparticles and in nanotubes themselves are comparable in the hydrogenated SNT product. The fact that temperatures and desorption rates of hydrogen from the hydrogenated SNT and GNF are close to each other allows one to assume that the bonding character between hydrogen and carbon in the SNT and GNF, as well as the mechanism of hydrogen release can be similar.

In summary, the interaction of carbon nanomaterials with hydrogen at high pressures and temperatures has given rise to the thermally stable compounds containing up to 6.8 wt % of hydrogen, most part of which is in the new state characterized by the absence of the C–H bands in the IR spectra.

This work was supported by the Russian scientific and technical program “Fullerenes and Atomic Clusters,” the program of OFN of the Russian Academy of Sciences “New Materials and Structures,” and the Russian Foundation for Basic Research (project no. 02-02-16859).

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Translated by V. Sakun

SPELL: 1. graphene