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Hydrogen sorption properties of arc generated single-wall carbon nanotubes

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Abstract

Studies regarding the possible use of single-wall carbon nanotubes (SWNTs) as a hydrogen storage material have attracted considerable interest in the last years. However, a large discrepancy in the results reported by different scientific groups is evident, and many of the recent studies do not confirm superior H_2 adsorbing properties of SWNTs compared to more conventional carbon materials. Nevertheless, synthesis of SWNTs with different diameters and a development of techniques for purification and opening can contribute to the improvement of their H storage efficiency. In the present work, SWNTs were produced by arc evaporation of graphite electrodes with the use of two different catalysts, 3Co/Ni and YNi_2. A three-step purification technique allowed enrichment of the samples with SWNTs reaching a level of purity exceeding 75%. In carefully performed sorption experiments on purified samples, reversible storage capacity of 2.4 wt.% H_2 was observed at cryogenic temperatures below −150 °C and at a pressure of 25 bar H_2. Thermal desorption studies revealed the presence of weakly bonded physisorbed hydrogen (90%) and chemically bonded hydrogen (10%). The latter was released at temperatures above 450 °C as a result of breaking of the covalent C–H bonds.

Keywords: Carbon nanotubes; Hydrogen storage materials; Electron microscopy

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1. Introduction

Carbon inhabits a multitude of different morphologies, among them the single-wall nanotubes (SWNTs). SWNTs can be produced by arc evaporation of metal–graphite electrodes. The yield of SWNTs in the products of evaporation depends on the catalyst used, parameters of electric discharge, gas composition and its pressure [1]. Condensed products formed by arc evaporation of metal–graphite electrodes are multiphase and contain, in addition to SWNTs, a number of different components including amorphous carbon, fullerenes, multiwall nanotubes, graphite-like and metal nanoparticles. Therefore, isolation and purification of SWNTs are necessary, and the most time-demanding steps in their production.

The available literature data concerning hydrogen sorption capacity of carbon nanomaterials are rather conflicting [2,3]. At ambient temperatures and pressures the H_2 sorption capacity of similarly prepared SWNTs spans the range from ~8 wt.% [4], down to <1 wt.% H_2 [5]. Several groups have reported a correlation between the amount of adsorbed H_2 in carbon nanomaterials and the specific surface area [6,7] and the micropore volumes [8] of the sorbents. The sorption capacities observed do not exceed the values reported for other carbon materials with high surface area (e.g., AX21 activated carbon obtained by chemical treatment of coke [9]). The main conclusion from these studies is that the H_2 uptake is due to a physisorption process, and that a considerable room-temperature H_2-storage does not take place in SWNTs.

Specific structure of the micropores in the sorbent may be an important factor in controlling the amount of physisorbed H_2 [8]. Thus, engineering of SWNTs by controlling tube diameters and tube–tube arrangements may still contribute to the establishment of the superior properties of SWNT carbon sorbents compared to the activated carbons.

Apart from differences in the structure of the materials

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used by different authors, sample weight, degree of purity and $P-T$ conditions, an additional source of the disagreements in the reported storage capacities of carbon nanomaterials could lie in inappropriate techniques of measurements. The major sources of errors are incorrect volume calibrations, first of all introduced by the contributions from a not properly determined density of the sample. For high-pressure experiments, a proper thermal management of the measurement system (avoiding temperature fluctuations and taking into consideration the exothermal effects from the introduction of pressurised gas into the reactor, and the temperature increase as a result of the adsorption processes) should be achieved.

In the present paper we report structural characteristics of SWNTs synthesised at IPCP RAS by electric arc evaporation of carbon rods containing a 3Co/Ni mixture or YNi_2 as catalysts. The work was aimed to characterise hydrogen storage properties of the purified SWNT and to establish a relation between their structure and H_2 sorption capacity. Thermal desorption spectroscopy and three different volumetric apparatuses were used in the measurements.

Table 1
Characteristics of process of synthesis of SWNT for two types of catalysts

Comparison parameter	Catalyst		
	Ni–Co	Ni–Y	–
Metal content in anode, at.%	0.64+1.9	1.9+0.95	–
Metal content in anode, mass %	11.2	14.4	–
SWNT yield (%) in ‘collar’ soot	15–20	30–50	–
SWNT yield (%) in ‘wall’ soot	2–3	10–15	–
Mass (g) of ‘collar’ soot	0.8–1	0.4–0.7	–
Mass (g) of ‘wall’ soot	3–3.5	0.8–1	–
SWNT diameter, nm	~1.2	1.3–1.5	–
Fullerene content of soot, %	~10	<1	20
Electrode gap, mm	2.5–3	1–2	0.5
Time for electrode evaporation, min	~50	12	45
Helium pressure, Torr	650	500	600
Current intensity, A	93	98	115
Rate of C evaporation, g/min	~0.2	~0.8	~0.3

2. Experimental details

2.1. Synthesis and characterisation

Synthesis of SWNTs was carried out by the arc-discharge method. Mixtures of cobalt and nickel powders (ratio 3:1) or YNi_2 powder prepared by a hydrogen decrepitation technique [10] were used as catalysts. Products formed by arc evaporation of the metal–graphite electrode were condensed on the lateral walls of the water-cooled chamber (‘wall’ soot), around the cathode (‘collar’ soot) and directly on the cathode (‘deposit’). It appears that the specific catalyst significantly influences the characteristics of the process of synthesis (see Table 1 for details).

The carbon samples were prepared for transmission electron microscopy (TEM) measurements (CMS, UiO) first by suspension in acetone, then by grinding and depositing on a copper grid.

2.2. Hydrogen sorption measurements

Hydrogen with a purity of 99.9999% was used in the measurements. H_2 sorption–desorption characteristics were measured at two laboratories; at IFE (Kjeller, Norway) and at IPCP RAS (Chernogolovka, Russia). Three volumetric setups were used. At IFE the experiments were performed using a volumetric setup with a rather large volume of 96 cm^3 in the pressure range 0.001–35 bar H_2, where, in addition, thermal desorption spectroscopy (TDS) measurements can be performed. At IPCP RAS a similar volumetric setup (volume of 53 cm^3) was employed working at H_2 pressures up to 50 bar. The third setup (volume of 7 cm^3) used at IFE and described in [11] allowed to measure precisely hydrogen adsorption–desorption isotherms in the pressure range 0.001–25 bar H_2 at temperatures of -196 to 200 °C.

The compressibility factor used in the volume determinations was obtained by fitting available low-temperature experimental data by an empirical equation as described in Ref. [12].

Before performing the measurements of H_2 sorption properties of the SWNTs, the samples were evacuated by a turbo molecular pump at pressures lower than 10^{-4} mbar (IFE) at $T=400$ °C and by a rotary pump at pressures lower than 10^{-2} mbar (IPCP RAS) at $T=200$ °C. After treatment for 1 h no more traces of desorbed gases were observed. The measurements were repeated at least three times using different combinations of connected buffer volumes. Mass of the samples studied was ~100 mg (IFE) and ~1000 mg (IPCP RAS).

3. Results and discussion

3.1. Synthesis, isolation and purification of SWNTs

Experiments on evaporation of graphite in presence of 3Co/Ni catalyst showed that the largest yield of SWNTs is reached under the following conditions: current 93 A, helium pressure 650 Torr (0.867 bar), average electrode gap 2.5–3 mm (sample 1). Table 1 presents further details.

Raman spectroscopy study of ‘collar’ soot indicated that the average diameter of SWNTs is ~1.2 nm, which agrees well with the data from the TEM study. Oxidising thermogravimetry showed that the soot contained ~50 wt.% of amorphous carbon, ~15 wt.% SWNTs and ~10 wt.% of graphite-like particles.

Optimum conditions for the synthesis of SWNTs with the use of YNi_2 as a catalyst (sample 2) differ substantially from using 3Co/Ni (see Table 1). The amount of SWNTs in the 'collar' soot of sample 2 becomes much higher in comparison with sample 1. The diameters of the nanotubes produced with YNi_2 catalyst (~1.4 nm) are larger compared to the SWNT produced with 3Co/Ni catalyst, as shows an analysis of the Raman spectrum of the soot in the region of the 'breathing' mode. Analysis of the data presented in Table 1 shows that the presence of yttrium forming thermodynamically stable carbides at high temperatures >1000 °C, suppresses the process of synthesis of fullerenes and facilitates the process of growth of SWNTs.

Isolation of SWNTs from the condensed products formed on electric arc synthesis was performed according to the scheme given in Fig. 1. This purification procedure includes several consecutive stages of acid treatment and thermal oxidation in air. After such a treatment open nanotubes become the major part of the sample. From the initial soot containing only ~10% of SWNTs, application of such a procedure yields a material containing ~75 wt.% SWNTs. Oxidising thermogravimetry also indicated the presence of graphite-like nanoparticles (~15 wt.%) and metal nanoparticles (~10 wt.%). TEM investigations presented the evidence of the formation of high purity SWNTs after completing all the purification stages. Fig. 2a and b show electron micrographs of 'collar' soot purified using a single stage of acid treatment and thermal oxidation in air. One can see that the sample still contains a large amount of amorphous carbon, metal (mainly Co) and graphite-like particles (Fig. 2a). The metal particles are covered with polycrystalline graphite in a matrix of amorphous carbon (Fig. 2b). The presence of Co/Ni, amorphous carbon and graphite was confirmed by synchrotron diffraction data (SNBL, ESRF, Grenoble). Fig. 2c shows a SWNT sample after completing all the stages in the purification procedure. The SWNTs form bundles consisting of 10–50 nanotubes of ~1.2 nm in diameter (Fig. 2d).

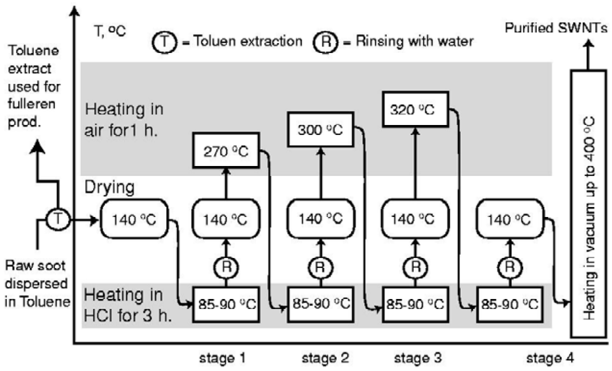

Fig. 1. Scheme of the process used for the isolation and purification using altering steps of acid treatment and thermal oxidation of SWNTs from the product formed during the evaporation of the YNi_2- or 3Co/Ni-graphite electrodes.

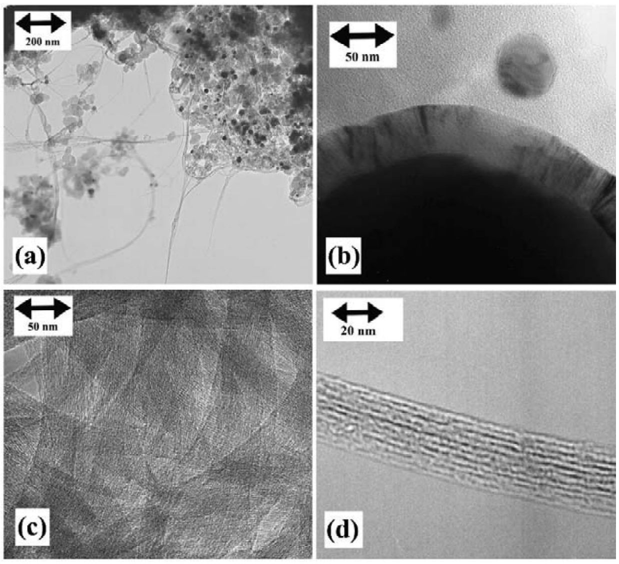

Fig. 2. TEM micrographs of SWNTs produced with 3Co/Ni as catalyst: (a) material containing SWNTs purified with one cycle of acid treatment and oxidation in air; (b) a single metal particle covered with carbon; (c) purified SWNTs; (d) bundle of SWNTs.

3.2. Hydrogen sorption properties

Hydrogen sorption properties were studied on purified SWNT samples. For the accurate hydrogen sorption studies, SWNT sample 1 synthesised with the use of 3Co/Ni as catalyst was chosen as it did not contain any hydride forming metals (yttrium, YNi_2 and yttrium carbides [13] are known to form hydrides). Fig. 3 presents the adsorption–desorption isotherms at liquid nitrogen temperature. This pressure–composition–temperature (P–C–T) measurement performed at IFE shows that the storage capacity gradually increases with pressure and reaches its

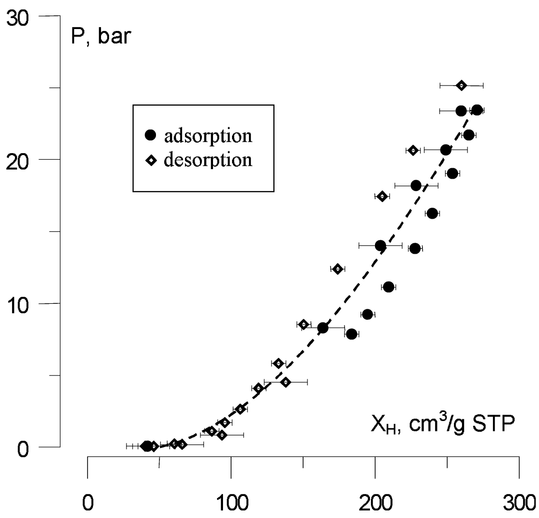

Fig. 3. Hydrogen sorption and desorption isotherm by SWNTs at $T = -196$ °C.

highest value of 275 cm^3/g STP or, equivalently, 2.4 wt.% H_2 at the highest applied pressure (25 bar). Saturation of the sample with hydrogen is not reached at this pressure. Experiments performed at IPCP RAS ($T = -196$ °C, pressure of 50 bar H_2) showed that the hydrogen sorption capacities of SWNTs prepared using 3Co/Ni catalysts were slightly inferior to SWNTs prepared using YNi_2 as catalyst, the latter sample storing ~15% more H_2. This indicates that tubes with larger diameter are preferable for hydrogen sorption. However, the contribution of the metal hydride forming impurities in the samples must be studied further before a final conclusion concerning the exact values of their sorption capacity can be drawn.

Measurements carried out using the IFE experimental setup with a larger volume show that an increase of hydrogen pressure from 25 to 35 bar at $T = -196$ °C results in an approximate doubling of the hydrogen sorption capacity. Besides, these measurements show that physisorption of H_2 takes place only near liquid nitrogen temperature, and the hydrogen sorption capacity sharply decreases when the temperature increases up to −130 °C (to about one tenth of the storage capacity at liquid N_2 temperature). For higher temperatures the capacity slowly decreases with increasing temperature. At room temperature, residual hydrogen sorption capacity is reduced to 0.2–0.4 wt.% H_2 (pressures of 10–30 bar H_2) and becomes relatively insensitive to pressure.

Fig. 4 presents traces of hydrogen desorption under dynamic vacuum conditions. Two desorption events are observed, a low temperature peak at approximately −160 °C and a high temperature peak at ~470 °C. The total quantity of desorbed hydrogen is about 50–60 cm^3/g STP; about 2/3 of this quantity is released above room temperature (~ 0.3 wt.%). The TDS data correlate well with the (P–C–T) measurements, according to which hydrogen sorption capacity of the carbon nanomaterial at liquid N_2 temperature and P_{H2}~0.1 bar is about 60–70 cm^3/g STP. The low temperature desorption peak is due to evolution of the physisorbed H_2. The high temperature desorption peak shows presence of rather strongly bonded hydrogen. Similar 'strong' hydrogen bonding has been observed in graphite ball-milled in H_2 atmosphere [14] in sorption studies of ball-milled SWNTs [15] and in the hydrogenated fullerenes [2,16] (e.g. $C_{60}H_{18-36}$). This strongly bonded hydrogen is identified as chemically bonded via a formation of C–H bonds. Such bonds are created due to the occurrence of C=C double bonds in the carbon pentagons present in the defects of the SWNTs. Furthermore, strongly bonded hydrogen is probably also located at the graphene edges created at the opened tube ends.

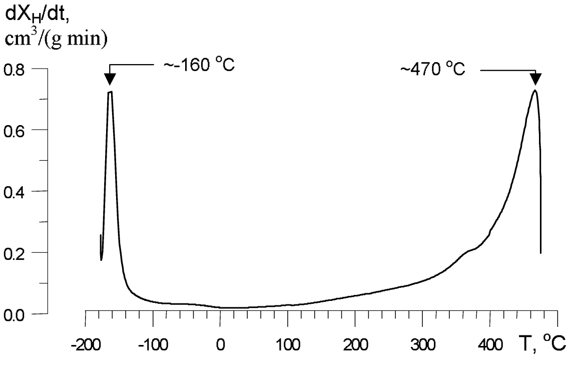

Fig. 4. Hydrogen thermal desorption under dynamic vacuum conditions (heating rate 2 °C/min).

Finally, this work shows that the pressure dependence of the H_2 storage capacity of the SWNTs near liquid N_2 temperatures is much more pronounced compared to the result reported by Chahine and Bose [9] for activated carbons. Indeed, at pressures below 25 bar there are no significant differences between the SWNTs and regular grade carbons. High surface area carbon (AX21 activated carbon) is even exhibiting superior H_2 storage properties. However, at higher pressures and cryogenic temperatures the situation is changed in favour of SWNTs. This can be explained by a pressure-induced increase in the tube–tube distances resulting in a larger surface area accessible for adsorption as suggested by Ye et al. [17].

4. Conclusions

The use of YNi_2 catalyst allows the synthesis of SWNTs with larger diameters as compared to the SWNTs produced with 3Co/Ni catalyst. It also suppresses the formation of C_{60}/C_{70} fullerenes. A purification procedure including alternation of acid treatment and thermal oxidation in air allows obtaining open-ended nanotubes with purity greater than 75 wt.%.

High purity SWNT samples can store significant amounts of H_2 only near liquid N_2 temperature. However, for pressures less than 25 bar H_2, the H_2 storage capacity does not exceed the values observed for other forms of carbon materials with high surface area. A sharp increase in hydrogen sorption capacity takes place near liquid N_2 temperatures and at $P > 25$ bar H_2. A small fraction of the stored hydrogen is chemically bonded and is liberated only upon heating the sample at temperatures above 450 °C.

SWNTs with larger diameters, ~1.4 nm, have higher H_2 storage capacity compared to the sample with smaller diameter of nanotubes, ~1.2 nm. Further studies are needed to examine in more detail such a relation and, also, to understand the influence of catalytic particles on the synthesis of SWNTs and their H_2 sorption behaviour.

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