# EVOLVED GAS ANALYSIS OF HEAT-TREATED CARBON NANOMATERIALS

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## Introduction

Physical and chemical sorption of small molecules by high specific surface area carbon nanomaterials readily occurs during their synthesis, purification and storage. Trapped molecules can affect material properties. For example, gas desorption from carbon nanotube field emitters leads to inferior performance and shorter life time of vacuum electronic tubes. Adsorbates on carbon nanomaterials can reduce the capacity of hydrogen storage devices. Therefore, the gas composition and quantity evolved by carbon nanostructures at elevated temperatures merits critical evaluation.

This paper presents data on evolved gas composition, which occurred upon heat treatment of fullerites, single-walled and multi-walled nanotubes. Variation of sorption properties upon chemical modification of nanostructures is discussed.

## Experimental

Mass-spectra of the gases eliminated from the specimens under elevated temperature were taken on mass-spectrometer MI-1201B (Sumy, USSR). The gas in ion source was ionized by electron impact (electron energy 70eV). Samples were placed in the quartz ampoule equipped by adjustable heater and connected through the needle valve with inlet system of mass-spectrometer. The sample was pumped out during one day up to the pressure $2x10^{-5}$Pa to remove weakly bounded surface impurities and contamination. Then the ampoule with the sample was isolated from the pumping system heated and kept at the temperature $T_1$ for 3 hours. Finally the needle valve was opened and the gases evolved from the sample were analyzed by mass-spectrometer. This procedure including pumping and heating was performed required (n) times at the temperatures $T_1<T_2<\ldots<T_n$.

## Results

Upon prolonged storage in air and heating to 65 °C the highly pure fullerite $C_{60}$ mainly evolves oxygen gas while deuterofullerite $C_{60}D_{18}$ almost exclusively evolves water molecules (fig.1 [1]). Above 400 °C the deuterofullerites evolve $CD_4$ and minor amounts of $C_2D_4$, and at 500 °C some deuterobenzene $C_6D_6$ was also found in the gas phase [2].

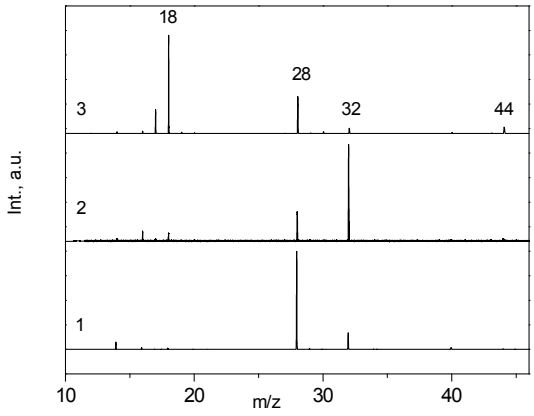


*Fig.1. Mass spectra of air (1) and the gases released from the fullerite $C_{60}$ (2) and deuterofullerite $C_{60}D_{18}$ (3) samples heated to 65 °C*

Arc produced multi-walled carbon nanotubes will, at temperatures up to 120 °C, evolve the hydrocarbons adsorbed from chemical laboratory air during storage. At higher temperatures (120-300 °C) the gases evolved consist of carbon monoxide and water.

Single-walled carbon nanotubes (SWNT) used in EGA studies were produced in the arc using Ni/Y or Co/Ni catalysts. As-produced materials with ~ 15 wt. % SWNTs were purified of amorphous carbon and metals by repeated oxidation in air at temperatures up to 550 °C and hydrochloric acid treatment to yield ~ 85 wt.% pure nanotubes. Purified SWNTs below 100 °C evolve mainly diethyl ether (ion $[CH_3O]^+$) and acetone molecules (Fig.2). Both solvents were used in purification. Hydrogen-containing molecules disappear from the mass-spectra upon heating the sample above 200 °C. On heating SWNTs to 500-560 °C the evolved gas is dominated by CO and $CO_2$ molecules.

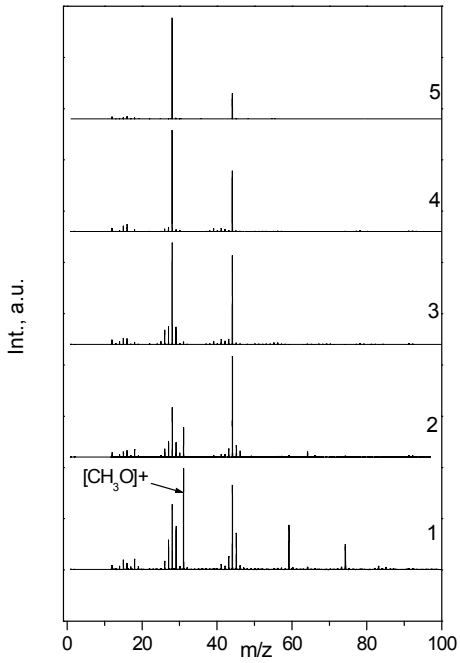


*Fig.2. Mass spectra of the gases released from the SMNTs heated to 100 (1); 200 (2); 400 (3); 500 (4) u 550°C (5).*

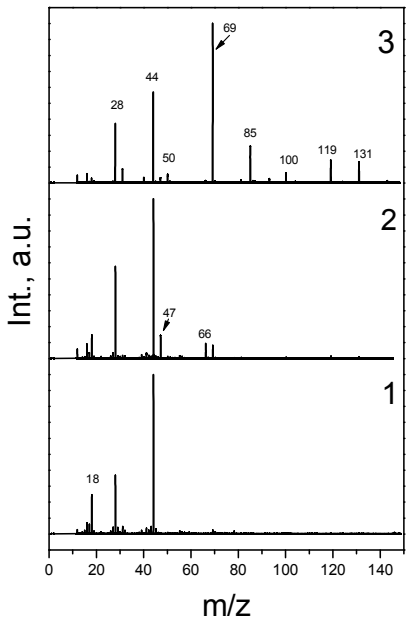


*Fig.3. Mass spectra of the gases released from the fluorinated MWNTs heated to 20-120 °C (1), 120- 300 °C (2) and 300 – 450 °C (3).*

Treatment of SWNTs that were stored in air by 1 MPa of deuterium gas at -180 °C does not alter evolved gas composition and behavior [3].

Purified SWNTs treated with 9 GPa of deuterium gas at 450°C contain more than 10 wt.% of deuterium when kept at these conditions [4]. It was found that from RT to 400°C the mass-spectra of gases evolved from so-treated nanotubes show mainly hydrocarbons and at 500-550°C mainly $D_2$ and HD molecules. Lower temperatures for hydrocarbon evolution compared to deuterium molecules indicate weaker bonding of hydrocarbons or their precursors to the nanotube skeleton. Both hydrocarbons and deuterium are likely chemically bound to the tube before the thermal cracking of C-C and C-D bonds releases gas molecules. Of note, the hydrogenated SWNTs readily absorb water vapor from air, much in preference to molecular oxygen.

Fluorinated MWNTs heated in vacuum (fig.3.[5]) from 20 to 120 °C mainly evolve $CO_2$, CO and $H_2O$. In 120-300 °C range the $COF_2$ molecules also evolve, and $CF_4$ and $C_2F_6$ molecules were found over fluorinated nanotubes at 200-450 °C.

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