Microwave Irradiation of Pristine Multi-Walled Carbon Nanotubes in Vacuum

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The goal of the present paper was to study the behavior of commercially available pristine multi-walled carbon nanotubes (MWNTs) under microwave irradiation (exposures up to 200 s) in vacuum, by means of several experimental techniques. An intense glow and heating of the nanotube samples were observed. Raman spectra, scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) images of the processed nanotubes did not show considerable changes as compared to those for pristine MWNTs. Closer structural investigation by means of conventional and high-resolution transmission electron microscopy (TEM and HRTEM, respectively) revealed an increase in the occurrence of open nanotube ends, whereas the sidewalls remained generally unchanged. The possibility of increase in the number of entry ports for gases was verified by employing temperature programmed desorption experiments with mass spectrometric detection (TPD-MS) with pristine and microwave-irradiated MWNTs exposed to atmosphere. The overall adsorption capacity did not change, whereas the rate of adsorption increased roughly by twice for the nanotubes irradiated for 200 s as compared to pristine MWNTs, which is consistent with selective opening of the nanotube ends.

Keywords: Multi-Walled Carbon Nanotubes, Pristine, Microwave Irradiation, Vacuum, Electron Microscopy, Gas Adsorption/Desorption.

1. INTRODUCTION

The rich chemistry of carbon nanotubes[1] (CNTs) can be induced by several energy sources. In addition to the common heating, a number of methodologies for the modification of CNTs were suggested based on electron and ion irradiation,[2] sonochemical,[3] mechanochemical[4] and microwave treatment.[5] Among these, the microwave approach gains especially wide recognition since it allows for the convenient combination of numerous possible chemical reagents for CNT functionalization with ready accessibility of microwave sources, which can be not only specialized scientific magnetrons but also ubiquitous household microwave ovens.

Indeed, numerous studies published during the last few years demonstrated that a number of important goals within the CNT chemistry can be achieved by using this energy source. The most basic and primordial one is CNT oxidation with strong acids and purification. It was shown that microwave digestion has a tremendous advantage as compared to the conventional purification techniques, since the acid can absorb microwave energy rapidly and dissolve metal catalyst and carbonaceous impurities efficiently without damaging the nanotube sidewall structure, and the processing time can be dramatically reduced;[6–8] this technique can be successfully applied to both single-walled and multi-walled CNTs (SWNTs and MWNTs, respectively). During microwave acid digestion, an inevitable process is CNT oxidation and formation of different oxygen-containing functionalities

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(mainly carboxylic group), which can be a separate goal since such groups are highly hydrophilic and thus improve CNT dispersibility in aqueous media.[9–11] An interesting recent finding is the possibility of selective removing metallic SWNTs by means of high-power microwave heating of dry SWNT powder;[12] the metallic nanotubes are burned more rapidly than the semiconducting nanotubes, producing high-purity semiconducting SWNTs necessary for sensor and electronic applications.

A large variety of hybrid nanomaterials can be synthesized by combining CNTs with inorganic and organic reagents under microwave treatment. The first inorganic species to mention are metal nanoparticles such as nickel,[13] gold,[14] platinum,[15–17] rhodium,[18] bimetallic platinum–cobalt[19] and platinum–ruthenium,[20, 21] with the particular applications mainly targeted to electrocatalysis in direct methanol fuel cells.[15, 17, 19–21] Other examples of inorganic nanohybrids of CNTs include tin,[22] cerium,[22] manganese[23] and lanthanum oxides,[24] as well as zinc sulfide.[25] As was noted by different authors, the advantages of microwave processing are that it is accelerated without significantly affecting a uniform nanoparticle size and shape, as compared to conventional refluxing.

Microwave-induced organic functionalization of CNTs was achieved by employing the reactions of 1,3-dipolar cycloaddition,[26–29] addition of diazonium salts[27, 30] and alkylhalides to the nanotube sidewalls,[31] as well as amidation of their oxidized defects.[28, 32] The efficiency of microwave-induced CNT chemistry was demonstrated again. For example, the amidation was completed in two steps as compared to three steps in the conventional approach.[28] The cycloaddition was completed in 15–60 min under microwave conditions, with the results similar to those achieved in 5 days using conventional methods.[28, 29] As short treatment time as several minutes was required for the microwave-induced electrophilic addition of alkylhalides to SWNTs.[31]

Last but not least are CNT composites with organic polymers. The vigorous response of MWNTs to microwave heating was used to locally melt a plastic matrix adjacent to the nanotubes within a few seconds, which resulted in the MWNT intercalation into polymer without any visible physical damage to the latter.[33] This "microwave welding" approach was suggested as a new paradigm for the formation of very strong CNT–polymer bonds without the use of adhesives, which can be employed for the anisotropic alignment of CNTs in polymers, patterned field emitters/conductors/resistors for flexible electronics, and high-strength composites.[33–37]

All of the above are remarkable achievements. Nevertheless, a logical question emerges: what happens to CNTs in the absence of other chemical reagents, or gaseous/solid/liquid media which can act as chemical reagents—in other words in vacuum? Such a "blank experiment" could serve (and is indeed necessary) as a reference point for the works on CNT functionalization

using microwave energy. Unfortunately, relevant data are very scarce up to now: we are aware of only one published report,[38] according to which SWNTs display strong microwave absorption accompanied with bright light emission, intense heat release, outgassing, and nanotube reconstruction. At the same time, no similar experiments were reported for MWNTs, which are envisioned as much more practical material for most technological applications (in particular, for hydrogen storage[39]) due to their low cost and better availability, as compared to purified SWNTs.

The goal of the present paper was to study the behavior of readily available pristine MWNTs (which have a high degree of purity at the same time) under microwave irradiation in vacuum, by means of a series of experimental techniques.

2. EXPERIMENTAL DETAILS

We used MWNTs (95%+purity, diameter of 10–20 nm) as received from Nanostructured and Amorphous Materials Inc., USA. MWNTs were preliminary degassed at 120 °C and a dynamic vacuum of 0.1 Torr. For each simple we used 10 mg of MWNTs, which were sealed in Pyrex tubes under vacuum at room temperature.

MWNT samples were microwave-irradiated for 5 to 200 s (at 5 s step increments), plus one more sample irradiated for 2 s. Irradiation was performed using a household LG microwave oven operated at 2450 MHz and at full 1100 W power. The Pyrex tubes with MWNTs were placed in a horizontal position inside the oven, with MWNTs dispersed along the tube. This position reduces the heat localization due to irradiation, as well as is thought to reduce graphitization of MWNTs. In any event, the heating was very significant, causing the Pyrex tube melting if the continuous irradiation time exceeded 20 s; to avoid this, larger irradiation times were afforded by alternating microwave treatment for 20 s and cooling the samples under ambient conditions.

For Fourier-transform infrared (FTIR) analysis, pristine (blank experiment) and irradiated MWNT samples were dispersed in 2-propanol (99.98% purity from Sigma) and ultrasonicated for 10 minutes. The dispersions were dropped onto an IR-optical ZnSe window to uniformly cover its surface with MWNTs, then placed into a vacuum dissicator for 24 h to remove the solvent. FTIR spectra were recorded by using a Nicolet 5SX FTIR spectrophotometer under an atmospheric pressure of 560 Torr and room temperature.

Micro-Raman spectra were recorded under the same conditions, using a Thermo-Nicolet Almega XR Dispersive Raman instrument equipped with an Olympus microscope B×51. An Olympus objective (×10 magnification, numerical aperture of 0.25 μm) was used both for focusing the laser on the sample (a spot size of ca. 3 μm), and for collecting the scattered light in a 180° backscattering configuration. The scattered light was detected by

a charge-coupled device (CCD) detector, thermoelectrically cooled to −50 °C. The spectrometer used a grating (2400 lines/mm) to resolve the scattered radiation and a notch filter to block the Rayleigh light. The pinhole of the monochromator was set at 50 μm. The Raman spectra were accumulated over 25 s with a resolution of about 2 cm^{-1}. The excitation source was 532 nm radiation from a Nd:YVO$_4$ laser (frequency-doubled), and the incident power at the sample was of ~8 mW.

For scanning electron microscopy (SEM) imaging, a JEOL JSM-5900 instrument operating at 20 kV was employed. Transmission electron microscopy (TEM) studies were performed by using a JEOL JEM-1200EX/ASID instrument operating at 120 kV. For high-resolution TEM (HRTEM) observations, a JEOL JEM-2010F FASTEM instrument operating at 200 kV was used. Scanning tunneling microscopy (STM) imaging was preformed on a JEOL JSPM-5200 instrument in constant current mode at room temperature in open air, using freshly cut Pt-Ir wire probes and freshly cleaved highly-oriented pyrolytic graphite (HOPG) supports.

Temperature programmed desorption experiments with mass spectrometric detection (TPD-MS) were carried out as described earlier.[40, 41] The system was based on an MX-7304A mass spectrometer (Sumy, Ukraine), with a mass range of 2–360 Da, electron impact energy of 70 eV, and sensitivity of 10^{-8} g. When the Pyrex tubes were open and irradiated samples were transferred into TPD-MS system, MWNTs were inevitably exposed to atmospheric gases in an uncontrolled way, for different periods. Therefore, to bring all the samples to comparable conditions of TPD-MS experiment, a blank thermodesorption run was carried out to remove atmospheric components. After it, all the samples were exposed to air for a fixed time of 20 min in the first series of experiments, or overnight in the second series.

3. RESULTS AND DISCUSSION

Visual manifestations of the effect of microwaves on pristine MWNTs were seen from the very beginning. Usually bright white glow was observed, similarly to the one reported by Imholt et al.[38] The interrelation between MWNT sample amount and the entire Pyrex tube size, which can be appreciated from Figure 1, gives an idea of how intense is the emitted light. In addition to uniform glowing, many sporadic sparks along the whole sample were detected. The origin of glowing and sparks is not fully clear. From common considerations, one can suggest that the light effects are related either to chemical conversions in MWNTs (for example, decomposition of residual catalyst particles, rearrangements in the nanotube ends/sidewalls/defects, etc.), or to the well-known light emission from CNTs induced by electric field (a physical process which does not alter the nanotube structure). The
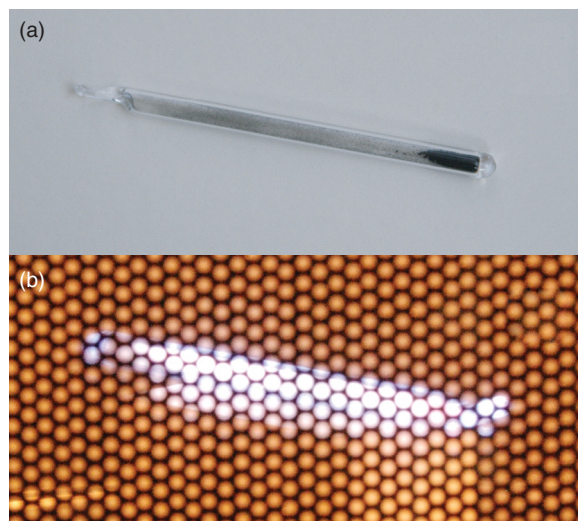

Fig. 1. Pristine MWNT sample in a seal Pyrex tube (a), and its glow upon microwave irradiation (b).

latter option seems to be more appropriate explanation, since the glowing can be observed even when irradiation-cooling cycles were repeated for several times, whereas any chemical process is expected to complete soon after irradiation was started.

To explain what happens to pristine MWNTs upon the action of microwaves, we characterized the irradiated nanotubes using FTIR and Raman spectroscopy, a number of microscopic techniques (SEM, TEM, HRTEM and STM), as well as studied the adsorption of atmospheric gases by means of TPD-MS.

FTIR spectra provided no useful information, mainly to their known poor quality for most kinds of CNTs (especially for the pristine nanotubes). On the contrary, Raman spectra measured showed all the most important features of the nanotubes. In particular, we observed the G-band around 1580 cm^{-1} (Fig. 2), which is similar to the G peak of graphite due to its basal plane, and corresponds to well-ordered rolled graphite sheets in MWNTs. The D-mode at about 1360 cm^{-1} is attributed to the defects or disordered structures in nanotubes. D band intensity was always higher, which is typical to pristine MWNTs. We compared G and D-band intensities, plotted as I_D/I_G in the inset to Figure 2. One can see that the nanotubes exhibit high stability even for long irradiation periods. The samples irradiated for short periods do not show any stable trend, but instead rampant changes in the I_D/I_G values. After ca. 50 s irradiation they stabilize and gradually increase, however the final I_D/I_G values do not exceed the original one for pristine MWNTs by more than 0.1 (that is 10%), thus indicating very slow changes in the nanotube sidewall structure.

Microwaves can induce currents not only in conductive carbon structures, but also in the residual catalytic metal particles, which close a significant fraction of the nanotube ends. Furthermore, the currents induced in metal
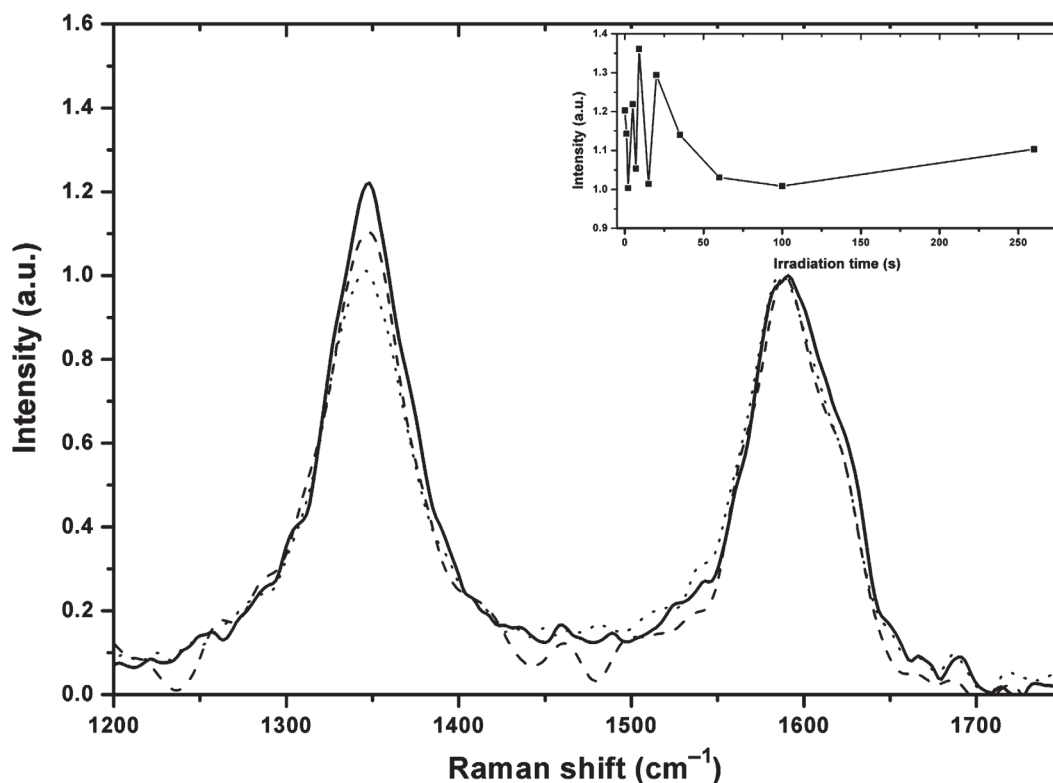
Fig. 2. Raman spectra of MWNTs: pristine (solid line), microwave-irradiated in vacuum for 20 s (dotted line) and 200 s (dashed line). The inset shows changes in the intensity ratio of D and G-peaks (I_D/I_G) as a function of microwave irradiation time.

would cause such a fast temperature rise that these particles would explosively evaporate. Since they are found mainly at MWNT ends, this phenomenon can selectively open the nanotubes without notably changing the sidewall structure, which was indeed evidenced by Raman spectroscopy. Another, more direct way to verify the state of irradiated MWNT ends and sidewalls is by using electron microscopy techniques. As a first approach, SEM showed no major alteration in MWNT aggregates (Fig. 3), but was incapable to reveal further structural details. For the latter purpose, we employed TEM and HRTEM methods. As one can see in the TEM image in Figure 4(a), no changes can be seen in the general nanotubular morphology. Dark spots are commonly observed at pristine MWNT ends, which are evidently due to the presence of residual metal catalyst particles. Similar spots can be found in the TEM image of MWNTs irradiated for 200 s (Fig. 4(b)), however in this sample they do not prevail: instead, open ends dominate.

Even though the above differences were less evident for short irradiation periods, HRTEM reveals numerous open ends (Figs. 5(a, b)) already in MWNTs irradiated for 2 s. They can be found along with seemingly intact closed ends (Fig. 5(c)). The sidewalls (Fig. 5(d)) look the same way as in pristine MWNTs and contain numerous imperfections, which explain the high-intensity D band at about 1360 cm^{-1} in Raman spectra (Fig. 2). After microwave irradiation for 200 s their number somewhat increases, as

can be seen in Figures 5(e, f). However, as a whole, the nanotubes keep their integrity.

One should note that prolonged observations by HRTEM at 200 kV and higher accelerating voltages can affect the nanotube structure and thus produce artifacts with consequent erroneous conclusions. We observed that MWNTs lose their tubular morphology, collapse and break when they are subjected to the high-energy electron beam
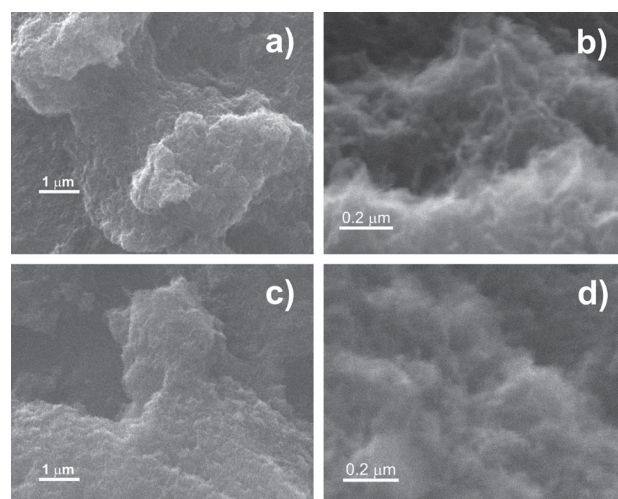

Fig. 3. SEM images at different magnifications of MWNTs: (a, b) pristine; (c, d) microwave-irradiated in vacuum for 20 s.
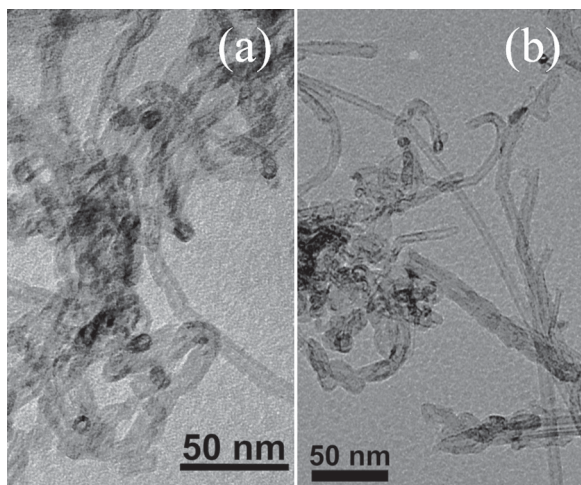
Fig. 4. TEM images of MWNTs: (a) pristine; (b) microwave-irradiated in vacuum for 200 s.

for a few tens of minutes; this is exemplified in Figure 6. The probability of such (undesirable in the present context) phenomena is higher for smaller-diameter nanotubes (less than 10 nm in Fig. 6) with considerable number of defects.
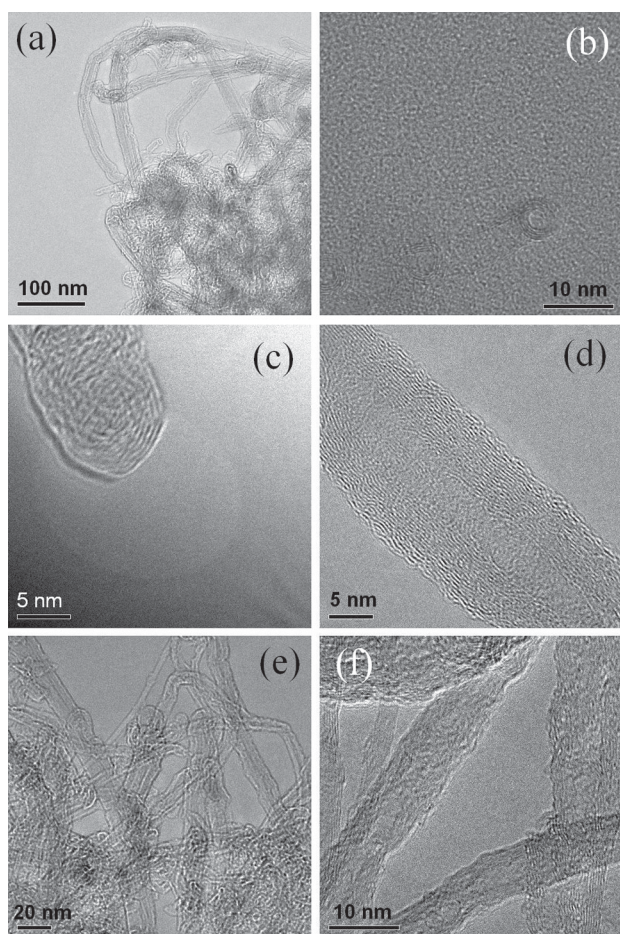

Fig. 5. HRTEM images of MWNTs microwave-irradiated for (a-d) 2 s and (e, f) 200 s.
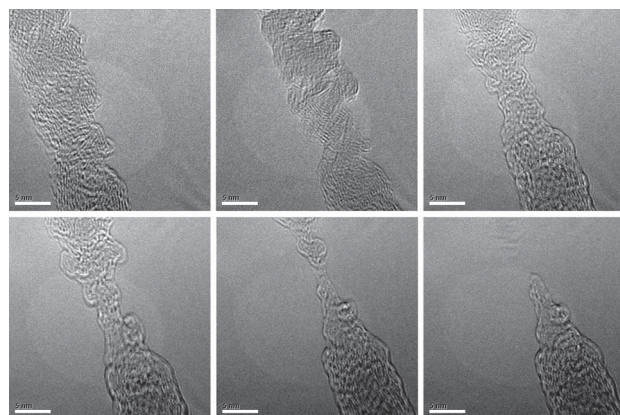

Fig. 6. Breaking MWNTs (sample microwave-irradiated for 2 s) during ca. 20-min exposure (images taken at ca. 4 min intervals) to 200 kV electron beam in HRTEM. Scale bar, 5 nm.

Therefore, HRTEM imaging has to be performed as fast as possible. Different types of electron irradiation-induced damage (shrinkage, collapse, welding, coalescence, etc.), are well documented (for a recent review see Ref. [2]); they are usually observed at higher accelerating voltages, within a few minutes of exposure, and the process starts at the innermost shells of MWNTs.

Despite of general capability of STM to achieve atomic resolution, in this particular case obvious technical difficulties were faced. The main problem is a strong trend of MWNTs to agglomerate, which makes virtually impossible a good-quality flat deposition of individual nanotubes onto HOPG. Even a prolonged ultrasonication is incapable to provide good dispersions of MWNTs, not to say that, similarly to high-energy electron beam, it is known to generate numerous defects and break the nanotubes. The images presented in Figure 7 show agglomerated MWNTs before and after microwave irradiation for 200 s. The nanotubes were suspended and thus easily moved with the probe, making it impossible to find differences in their sidewall structure. At the same time, the background around the irradiated nanotubes (Fig. 7(b)) does not exhibit numerous non-uniformities, contrary to what can be observed for pristine MWNTs (Fig 7(a)). This allows us to conclude that microwave processing removed small particles of impurities from the latter, which is in agreement with the reports[6–8] by other authors on the purification of CNTs using microwaves.

Opening the MWNT ends must provide additional entry ports to the inner nanotube cavities for small chemical species. In particular, one can expect that the capability of MWNTs to adsorb gases changes after microwave irradiation. In order to verify whether this is the case, we performed a series of temperature programmed desorption experiments with mass spectrometric detection (TPD-MS). When the sealed Pyrex tubes, in which MWNTs were subjected to microwave irradiation, were open and the samples were transferred into TPD-MS system, the nanotubes were
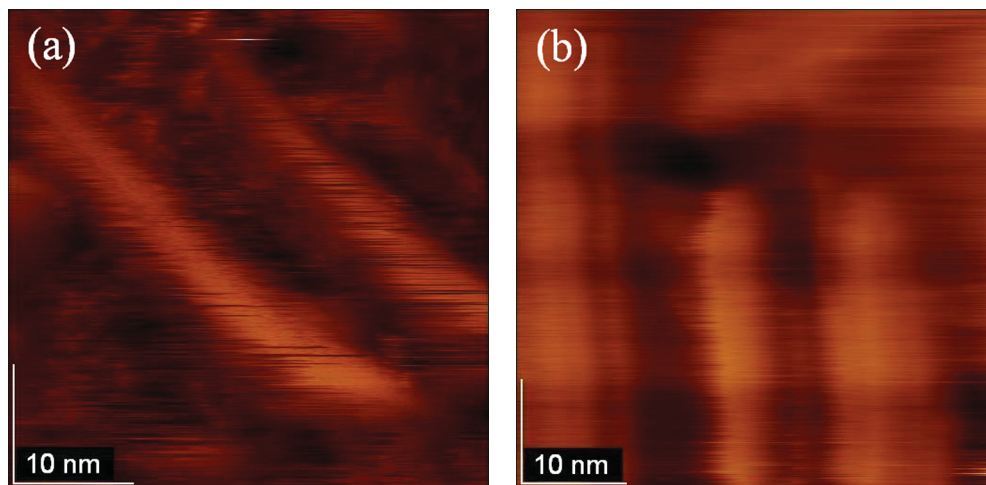
Fig. 7. STM images of MWNTs: (a) pristine (tunnel current 0.516 nA, bias voltage −0.256 V); (b) microwave-irradiated in vacuum for 200 seconds (tunnel current 0.503 nA, bias voltage −0.500 V). JEOL JSPM-5200 instrument operating under ambient conditions.

exposed to the atmosphere for different time for each particular sample. To provide identical conditions of TPD-MS experiment for all of them, a blank TPD run was carried out to remove adsorbed atmospheric components. Then all the samples were exposed to air for a fixed time of 20 min in the first series of experiments, or overnight in the second series. The thermodesorption of four atmospheric components was monitored, namely water, nitrogen, oxygen and carbon dioxide (molecular weight of 18, 28, 32 and 44, respectively). The results for the first series of measurements are shown in Figure 8. The height of the main H_2O desorption maximum after 100 °C increased roughly by twice for MWNTs irradiated for 200 s as compared to the pristine sample; MWNTs irradiated for 20 s occupy intermediate position. The shape of TPD curves for N_2 and

CO_2 changed after irradiation, where desorption maxima after 100 °C appeared versus almost flat uniform curves for the pristine nanotubes; in the case of oxygen, no evident changes can be seen. On the other hand, after the overnight exposure to air in the second series of experiments, the differences between the samples dramatically decreased, which can be seen from the comparison of TPD curves for pristine MWNTs and the sample irradiated for 200 s in Figure 9.

Our interpretation of the TPD-MS data obtained is as follows. The new open nanotube ends in the microwave-irradiated MWNTs allow for larger amounts of gases to enter. In the first series of experiments, the short air exposure time (20 min) did not allow for filling the nanotubes completely and reaching the adsorption equilibrium;
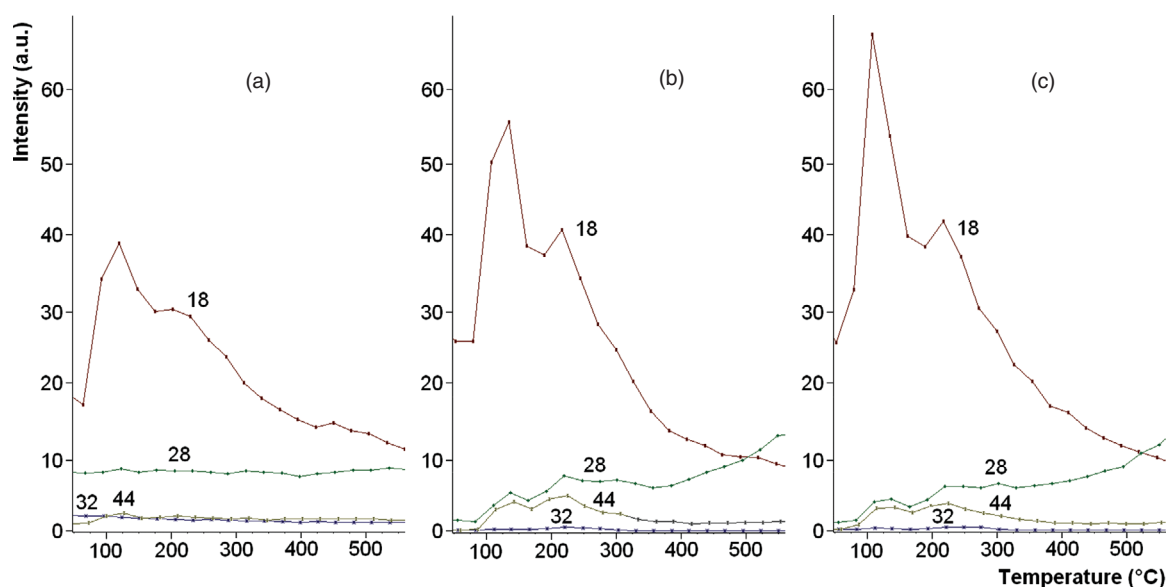

Fig. 8. TPD-MS thermograms of selected atmospheric components for MWNTs: (a) pristine; microwave-irradiated for (b) 20 s and (c) 200 s. After degassing in vacuum (blank TPD run), all MWNTs were exposed to air for 20 min. Atmospheric components: 18, water; 28, N_2; 32, O_2; 44, CO_2.
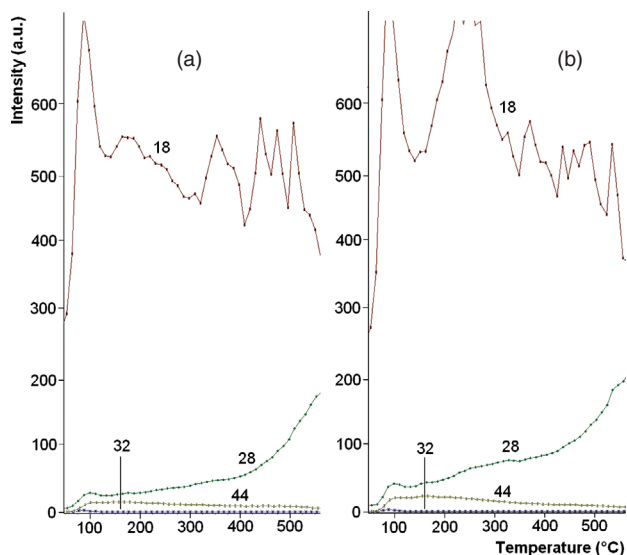
Fig. 9. TPD-MS thermograms for selected atmospheric components for MWNTs: (a) pristine; (b) microwave-irradiated for 200 s. After degassing in vacuum (blank TPD run), MWNTs were exposed to air overnight. Atmospheric components: 18, water; 28, N_2; 32, O_2; 44, CO_2.

therefore, the more open ends MWNTs had, the larger amounts of gases were adsorbed and correspondingly detected by TPD-MS. This situation changed with extending the air exposure overnight. In this case, the time was sufficient to reach adsorption equilibrium and to fill the nanotubes. However, the amount of adsorbed (and correspondingly desorbed) gases turned to be nearly the same for different samples, since the sidewalls (and correspondingly gas adsorption capacity of MWNTs) remained almost unchanged after microwave irradiation.

4. CONCLUSIONS

An intense glow and heating are produced under microwave irradiation (exposures up to 200 s) of pristine MWNTs in vacuum. Raman spectra, SEM and STM images of the processed nanotubes did not show considerable changes as compared to those for pristine MWNTs. Closer structural investigation by means of TEM and HRTEM techniques revealed an increase in the occurrence of open nanotube ends, whereas the sidewalls remained generally unchanged. The possibility of increase in the number of entry ports for gases was verified by employing TPD-MS experiments with pristine and microwave-irradiated MWNTs exposed to atmosphere. The overall adsorption capacity did not change, whereas the rate of adsorption increased roughly by twice for the nanotubes irradiated for 200 s as compared to pristine MWNTs, which is consistent with selective opening of the nanotube ends.

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