EFFECT OF CHANGE SELECTIVITY FOR SENSING ELEMENT MADE OF MULTI-WALL CARBON NANOTUBE NETWORK TREATED BY PLASMA

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Abstract

Multiwall carbon nanotubes (MWCNT) network called “Buckypaper” was made by the vacuum filtration method from MWCNT aqueous suspension. In this way we created multi-wall carbon nanotube (MWCNT) networks featured by randomly entangled pure nanotubes. These networks were applied as gas sensors for organic vapors of ethanol and heptane, polar and nonpolar solvents respectively. The gas response was investigated by electrical resistance measurements. The surface sensitivity and selectivity was then modified by low-temperature reactive surface plasma treatment in different gases. With plasma treatment, we first created the functional groups on the nanotubes surface and latter etch them. These processes changed surface selectivity for detection of organic vapors. The results showed that the MWCNT network electrical resistance increased when exposed to organic solvent vapors. This is reversible process, when removed from the vapors. Therefore, the MWCNT networks show the potential to be used as improved sensing elements for sensitive and selective organic vapor detection in near future.

Keywords: carbon nanotube network, sensor, buckypaper, electrical resistance, plasma treatment

1. INTRODUCTION

Single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) show remarkable sensitivity to the change of chemical composition of the surrounding environment. This property is favorable for their use in the form of membranes [1], adsorbents [2] or gas sensors [3, 4, 8] and pressure sensors [9, 10]. Gas and vapor adsorption as well as desorption usually proceeds at high rates and amounts [5]. The molecules are adsorbed on the carbon nanotube (CNT) surface by van der Waals attracting forces, which leads to remarkable changes in CNT electrical resistance. A smart application of this principle can eventually lead to development of CNT-based electrochemical biosensors and gas sensors with a useful ability to detect various gases and organic vapors. Conductivity measurement is then a simple and convenient method to register CNT response to vapor adsorption/desorption.

Previous research [6, 7] found that physisorbed molecules influence the electrical properties of isolated CNTs and also inter-tube contacts. The resistance of macroscopic CNT objects like aggregates or network structures used in gas sensors is predominantly determined by contact resistance of crossing tubes, rather than by resistance of CNT segments. Here, the tubes are much shorter than sensor dimensions and inter-tube contacts act as parallel resistors between highly conductive CNT segments.

The dominating process influencing macroscopic resistance is probably gas or vapor adsorption in the space between nanotubes, which forms non-conductive layers between the tubes. This process decreases both the quantity and quality of contacts between nanotubes and consequently increases macroscopic resistance [3].

Functionalizing the carbon nanotubes with a number of functional groups is known to increase their chemical reactivity and can be used as a starting point for further chemical modification. Several methods such as chemical, electrochemical, polymer wrapping, and plasma treatment have been applied to modify the CNT surface. The functionalization of CNTs can be made by using hydrogen, nitrogen, ammonia, O2/Ar, O2, CF4, or SF6 plasmas. [11]
The present work describes resistive gas sensors prepared in a simple way from MWCNTs. Their sensitivity to saturated vapors of two different organic solvents are tested. Finally, reversibility of adsorption/desorption cycles is tested for acetone.

2. EXPERIMENTAL

The purified MWCNT are produced in a high-yield catalytic process based on chemical vapor deposition were supplied by Bayer MaterialScience, Germany (diameter 5-20 nm, length 1-10 μm, purity >99% and number of walls 3-15. The MWCNT aqueous paste was prepared using a mortar and pestle (0.5 g of MWCNT and ~ 5 ml of deionized water), then homogenized using Dr. Hielscher GmbH apparatus (ultrasonic horn S7, amplitude 88 μm, power density 300 W/cm², frequency 24 kHz) for 2 hours and the temperature of ca 50°C. Then were added 3 ml Triton X-100 and 1-M aqueous solution of NaOH for adjusted pH to the value of 10. The dispersion was homogenized using Dr. Hielscher GmbH apparatus (ultrasonic horn S7, amplitude 88 μm, power density 300 W/cm², frequency 24 kHz) for 1 hour and centrifuged for 15 min at 3000 rpm. The sediment was removed.

MWCNT networks, “Buckypaper” (MWCNT-N), were prepared by dispersion vacuum filtration thought polyurethane submicron size porous membrane. The formed disk-shaped network was washed several times by deionized water and methanol in situ, then removed and dried between filter papers at RT. The resulting buckypaper was cut in the shape of strips. The strips were treated by plasma. Was used RF (radio frequency) O₂, CO₂, N₂, H₂, Ar, SO₂ and CF₄ plasma and pressure 50 pa.

The strips made of CNT networks were exposed to the vapors of two different solvents ethanol and heptane. The chosen solvents are characterized by their polarity. The specimens were exposed to saturated vapors of solvents at defined experimental conditions: 25 °C, atmospheric pressure and 6 minute adsorption/desorption cycles.

3. RESULTS

Fig. 1 represents SEM analyses of upper surfaces of prepared CNT networks. The surface of CNT networks is very smooth, clean without fragments in the space between the network.

![SEM analyses of CNT networks made by vacuum filtration.](image)

Fig. 1 SEM analyses of CNT networks made by vacuum filtration.

Fig. 2 represent the change of sensitivity of CNT networks treated by seven different gases. The modification create different functional groups on multiwall carbon nanotube surface. Each functional group has different affinity for polar and nonpolar organic vapors represent by ethanol and heptane.
Fig. 2 The sensitivity of Multiwall carbon nanotubes network exposed to vapors of two different organic solvents and treated by plasma in seven gases at 50pa and 3 minutes.

The typical adsorption/desorption behavior of CNT network exposed to/disposed from organic vapors is presented in Fig. 3. The graph illustrates a time-dependent change of parameter S representing sensitivity of the nanotube networks. The curves show specific course of adsorption/desorption, with an obvious on/off effect. An initial sharp increase in sensitivity is followed by a slower phase. Simultaneously, desorption is represented by a rapid decrease reaching a constant value in some cases, in others followed by further, slower decrease. The sensitivity is defined by eq. 1 where $R_a$ represents specimen resistance in air and $R_g$ resistance of the specimen exposed to gas/vapor, $\Delta R$ stands for the resistance change.

$$ S = \frac{R_g - R_a}{R_a} = \frac{\Delta R}{R_a} $$

(1)

Table 1 presents properties of tested organic solvents. Hildebrand solubility parameter, $\delta_t$, and pressures, $p_i$, and saturated vapor volume fractions, $x_i$. It was found that $x_i$ has the similar value for both solvents so the sensitivity depend on their polarity.

Table 1 Properties of tested organic solvents: Hansen solubility parameters, $\delta_d$, $\delta_p$, $\delta_h$ total Hildebrand solubility parameter, $\delta_t$, saturated vapor pressures, $p_i$, and corresponding volume fractions, $x_i$, at 25°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_d$ [Mpa$^{1/2}$]</th>
<th>$\delta_p$ [Mpa$^{1/2}$]</th>
<th>$\delta_h$ [Mpa$^{1/2}$]</th>
<th>$\delta_t$ [Mpa$^{1/2}$]</th>
<th>$p_i$ [kPa]</th>
<th>$x_i$ [vol. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>15.3</td>
<td>0</td>
<td>0</td>
<td>15.3</td>
<td>6.13</td>
<td>6.0</td>
</tr>
<tr>
<td>Etanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>26.5</td>
<td>7.86</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Fig. 3 Represents response to three consecutive cycles in saturated vapors of ethanol measured in 6-minute intervals. Experimental data also demonstrate good reversibility of adsorption/desorption processes.
Fig. 3 Three adsorption/desorption cycles of Multiwall carbon nanotubes network exposed to vapors of ethanol.

CONCLUSIONS

Multiwall carbon nanotubes were used to prepare CNT network (buckypaper) by vacuum filtration method. Their response to adsorption/desorption cycles were determined as a change of macroscopic resistance. The response to adsorption/desorption was measured as a change of resistance. The surface of buckypaper was treated by RF plasma in seven gases atmosphere, by this way was change of affinity for polar and nonpolar organic vapors. The lowest response was 7.86 % in SO$_2$ plasma and highest 13.20 in CF$_4$ for ethanol. The lowest response was 11.00 % in O$_2$ plasma and highest 14.44 in Ar for heptane. The sensitivity is not so higher because it is surface modification. In the future work will be treated the pristine multiwall carbon nanotube in powder state for better results. CNT network has good sensitivity and assumed selectivity defined by pressures of saturated vapors of used organics solvents. Finally it was found that measured response has good reversibility.

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LITERATURE


