Materials Letters 122 (2014) 281–284

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Humidity-sensing characteristics of multi-walled carbon nanotube sheet

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ARTICLE INFO

Article history:
Received 18 January 2014
Accepted 13 February 2014
Available online 19 February 2014

Keywords:
Multi-walled
Carbon nanotube sheet
Humidity sensor

ABSTRACT

The properties of humidity sensors made of spin-capable multi-walled carbon nanotubes (MWCNTs) were characterized and their sensing mechanisms analyzed. The results showed that their resistance increased linearly upon exposure to water molecules. Within the range of 10–90% relative humidity, the resistance of the MWCNT humidity sensor increased due to charge transfer. We found that the sensitivity and response time of the sensor could be improved by acid treatment. In addition, the surface area and contact number of MWCNTs played an important role in the improvement of sensor performance.

1. Introduction

The manufacture of a high-performance humidity sensor is rather complicated, as many requirements must be met to achieve excellent sensor characteristics, including linear response, high sensitivity, fast response time, chemical and physical stability, and low cost [1]. The use of carbon nanotubes (CNTs) in a humidity sensing layer has been investigated, and many papers have reported the development of a CNT-based sensor for humidity detection [2]. In general, CNT humidity sensors are made as individuals, bundles, or dispersed solutions of single or multi-walled carbon nanotubes (MWCNTs) on substrates that are functionalized by the addition of suitable polymer or metal oxide nanoparticles. There are two main methods for fabricating CNTs for use as humidity sensors. One is to directly grow CNTs between electrodes by chemical vapor deposition (CVD) [3]. The other is to drop-cast a CNT suspension (dispersion) or a CNT composite onto a polymer substrate with electrodes [4]. Although the latter method is relatively easier, it results in uneven dispersion of CNTs on the electrodes, which can worsen sensor performance. Moreover, the CNTs on these films have a low density and/or are random [5]. Accordingly, simple, inexpensive, high yield, and reproducible fabrication techniques should be employed for the successful fabrication of CNT-based sensors. On the other hand, our group [6–8] has previously reported MWCNT sheets fabricated from spin-capable MWCNT forests. These MWCNT sheets have a large surface area and show good adhesion to substrates. These properties have inspired us to use MWCNT sheets in humidity sensor applications. In this paper, therefore, a MWCNT sheet-based humidity sensor is proposed along with a simple, low-cost fabrication process that does not require manipulation of individual and/or bundles of CNTs or complex, expensive techniques such as photolithography.

2. Experimental details

Detail process of CNT growth and experimental procedure was described in supplementary data [9]. As shown in Fig. 1, the MWCNT sheets were directly pulled from a super-aligned MWCNT forest onto glass. This provides a very simple and easy method to fabricate the sensor. The acid treatment was conducted in solutions of H_2SO_4/HNO_3 (3:1, 50 ml) for 1 h at room temperature.

3. Results and discussion

It is well known that MWCNTs are hydrophobic, which means that the H_2O–MWCNT interaction is weak [10]. This results in the accumulation of few water vapor molecules on the surfaces of MWCNTs. It is also well known that acid treatment creates surface functional groups such as –COOH and –OH, which make the MWCNTs hydrophilic [11]. To investigate the effect of acid treatment, XRD and Raman spectroscopy measurements were employed. XRD and Raman spectroscopy indicated the graphite structure the surface modification, respectively. Fig. 2(a) shows the XRD patterns of MWCNTs. Some broad peaks can be observed in the range of 30–40 (2θ), which might be attributed to the defects and/or damage introduced by acid treatment. However, the XRD spectra shows predominant peaks at $2\theta = 26^{\circ}$ before and after acid

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http://dx.doi.org/10.1016/j.matlet.2014.02.049
0167-577X

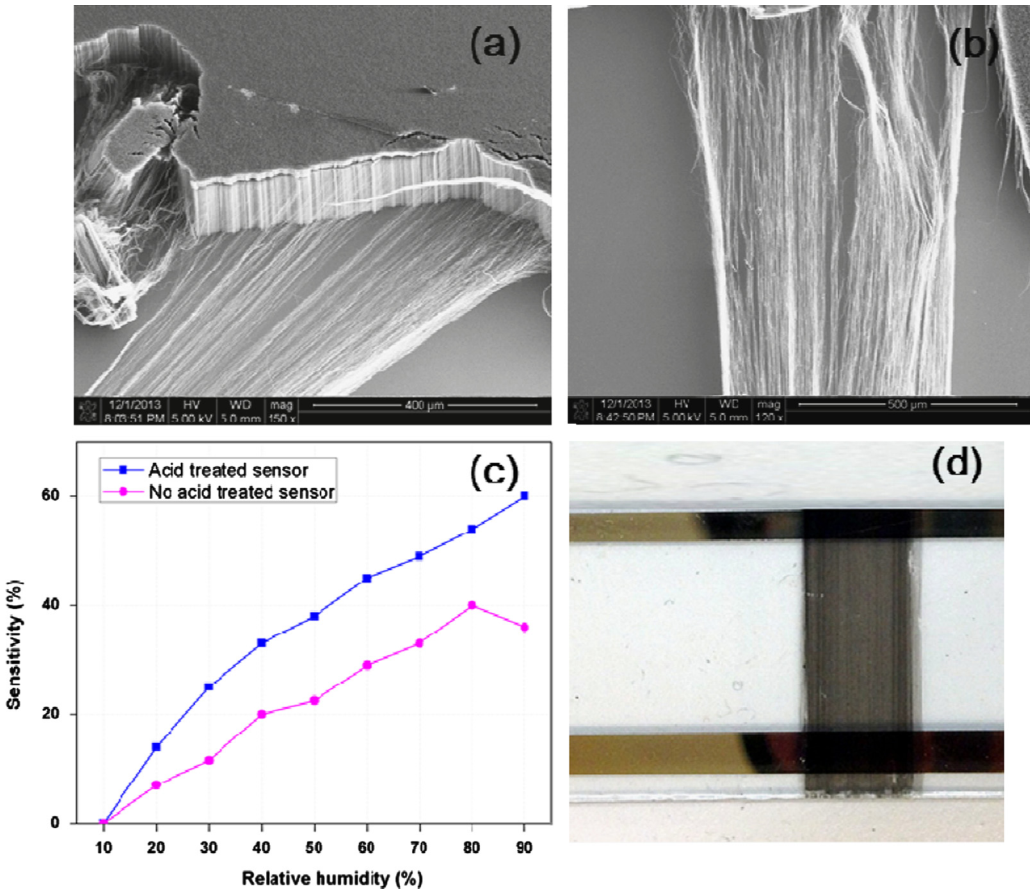

Fig. 1. SEM images (a) and a photograph (b) of CNTs sheet pulling from the CNTs forest, (c) sensitivities of the MWCNT-sheet humidity sensors as a function of relative humidity with respect to acid treatment, and (d) fabricated humidity sensor.

treatment, which means properties of MWNTs with highly structured graphitic carbon (002). Therefore, we note that no significant influence on the crystalline phase was observed after acid treatment. The Raman spectra of MWCNTs clearly show two sharp peaks at approximately 1325 cm^{-1} (D band) and 1596 cm^{-1} (G band) as shown in Fig. 2(b). The intensity ratio of the D to G bands (I_D/I_G) increased significantly upon acid treatment. This indicates that acid treatment lead to the creation of defects such as dangling bonds and oxygenated vacancy on the surfaces of the carbon nanotubes [12,13].

The sensitivity of the MWCNT sheet-sensor was determined using the following equation:

$$\text{Sensitivity}(\%) = (R - R_0)/R_0 \times 100 \quad (1)$$

where R and R_0 are the resistances at a given humidity level and 10% RH, respectively. Fig. 3(a) shows the typical humidity-sensing response of the sensors to different humidity levels ranging from 10% to 90% RH. The resistance of the MWCNT sheet-sensor increased upon exposure to H_2O molecules. The mechanism of the sensor could be described as follows. When a MWCNT sheet is introduced into a chamber with a certain humidity level, H_2O molecules are adsorbed onto the surfaces of MWCNTs. The amount of H_2O molecules that is adsorbed to the MWCNTs directly depends upon the RH level inside the chamber. During the adsorption process, electrons are transferred from H_2O molecules to the MWCNTs due to an electrical potential difference between the two materials. As the RH level increases, large H_2O molecules are adsorbed and more electrons are transferred. These transferred electrons actually constitute a minority carrier injection process, which should reduce the majority carrier concentration and increase resistance of the MWCNTs [14]. Thus, MWCNTs have a p-type property. Besides the electron donation model, other mechanisms of humidity sensing have been proposed. Pati et al. [15] studied the interaction of H_2O molecules with CNTs and demonstrated that H_2O molecules undergo physisorption onto the surfaces of nanotubes. This means that a weak bond is formed between an H atom of a H_2O molecule and a C atom on the surfaces of the nanotubes. Quantum conductance calculation shows that H_2O adsorption will inevitably increase the resistance of CNT-based materials. Thus, our obtained results are in line with the findings given by Pati's group.

On the other hand, the sensitivity of the MWCNT sheet-sensor without acid treatment decreased at RH > 80%, which was compensated for by other factors. We assume that a doping effect can explain this compensation [16,17]. When MWCNTs are exposed to a humid environment, p-type MWCNTs can absorb an excessive number of electrons, as the H_2O molecules serve as electron donors. In other words, the original p-type property of the MWCNTs can change to an n-type property beyond the threshold humidity level since the transferred excess electrons would completely cancel out the intrinsic majority holes. In our case, the threshold humidity level appeared at RH = 80%. Beyond this threshold, there was a reduction in the resistance of the sensor, which means that the property of the MWCNTs changed to an n-type semiconducting material. This inference is reasonable since the high humidity level caused the compensating doping effect. However, the MWCNT sheet-sensor with acid treatment showed defective sites (COOH) characterized by low-energy adsorption that provided more nucleation sites for electron transfer. Therefore, the sensor with acid treatment had higher and linear