Applied Surface Science 259 (2012) 159–165

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Preparation of nanosensors based on organic functionalized MWCNT for H_2S detection

F. Mohammadzadeh [a], M. Jahanshahi [a,*], A.M. Rashidi [b]

[a] Nanotechnology Research Institute, School of Chemical Engineering, Babol University of Technology, Iran
[b] Nanotechnology Research Center, Research Institute of Petroleum Industry, Tehran, Iran

ARTICLE INFO

Article history:
Received 24 May 2012
Received in revised form 1 July 2012
Accepted 2 July 2012
Available online 8 July 2012

Keywords:
Gas nanosensors
H_2S in natural gas
MWCNT
MWCNT-amines
Recovery

ABSTRACT

The effects of various organic functional groups on electrical responses of multiwalled carbon nanotube sensors for H_2S detection in natural gas (about 160 ppm) at different operating temperatures (25–80 °C) were investigated. The experimental results showed that the amino groups functionalized carbon nanotube nanosensor displayed good chemical sensitivity (25–30%) at room temperature because of —NH reactive sites on the tubes while MWCNT group had excellent performances at higher temperatures. The mechanistic of optimum conditions for functionalized MWCNT based nanosensors and their characterization are strongly going to be discussed.

1. Introduction

H_2S is a toxic, colorless and flammable gas at standard condition which causes human death, environmental hazards and industrial equipment corrosion even at low concentrations [1]. Besides sewage [2], volcanic gas and hot spring [3], natural gas (sour gas) and crude oil are the main sources of hydrogen sulfide which is the major problem in exploitation and transportation process, gas sweetening and recovering plants at gas refineries in oil reach countries specially in middle east. It is oxidized to sulfur dioxide by atomic oxygen, molecular oxygen or ozone during oil or gas combustion which pollutes the air [4].

Leakage of sour gases via gas transportation, sweetening processing and etc. which contains mainly methane and several ppm of H_2S, can cause human health hazards. According to the American Conference of Government Industrial Hygienists safety statements [5], the threshold limit of H_2S was defined as 10 ppm. Thus monitoring and detection of H_2S are very important for environmental safety and human health.

Semiconductor metal oxides (SMO) are used extensively in H_2S sensors [6,7]. Although they have good advantages in sensing of gas molecules such as long lifetime and low maintenance, the application of these sensors is limited to some disadvantages, for instance, poor selectivity, long response time, high operating temperature ranging from 200 °C to 400 °C or the limited detection range respect to CNTs [8–10]. It can be obviously seen that response and selectivity of sensors are drastically influenced by surface area and contact interfaces between target gas and sensing material. Marvelous interests in technical and scientific researches have been focused on carbon nanotubes due to their high surface area, nano structure and huge amount of available sites for adsorption and reaction of gas molecules which demonstrate their remarkable adsorption properties [11–13]. Adsorption of gas molecules on carbon nanotubes significantly affects their electrical behavior and makes them capable to act as a gas sensor. Various sensors have been built in accordance with different structures of nanotubes (single walled and multiwalled) and their sensing properties have been investigated at different operating temperatures especially at room temperature [14–16].

Many of current studies have been focused on investigation of single walled carbon nanotube sensors [17–19]. However, multiwalled carbon nanotubes have excellent properties and their lower production cost and possibility of generation at huge amount are attracting tremendous interests recently [20–22].

To improve sensing characteristics of nanotubes, they can be functionalized by different substances and via different functionalizing methods [23,24]. Functionalization causes debundling of carbon nanotubes and so increasing their surface area [25]. Various methods have been reported for functionalizing carbon

* Corresponding author at: Nanotechnology Research Institute, Babol University of Technology, Babol, P.O. BOX: 484, Iran. Tel.: +98 111 3220342; fax: +98 111 3220342.
E-mail addresses: mmohse@yahoo.com, mjahan@nit.ac.ir (M. Jahanshahi).
URL: http://www.nano.nit.ac.ir/IndexEn.aspx (M. Jahanshahi).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.07.011

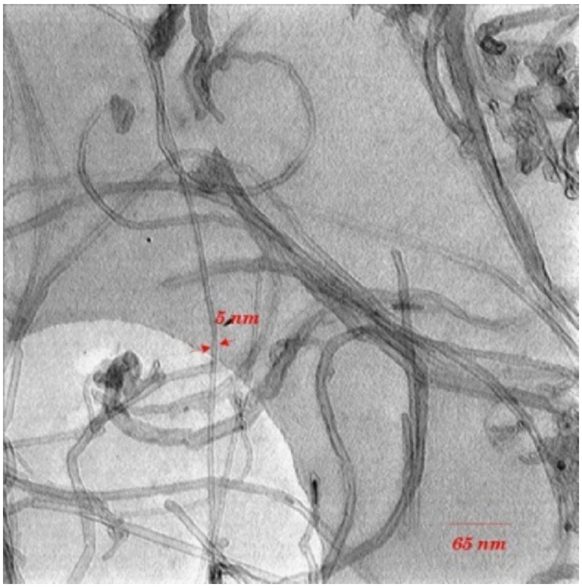

Fig. 1. TEM image of as grown CNTs.

nanotubes. Among them, amino-functionalized CNTs have been studied due to the fact that amino group has a high reactivity, a rich source of chemistry and can react with many chemicals [26]. Moreover, the purification technologies, i.e. the removal of acid gas impurities such as CO_2 and H_2S from the gas streams include chemical and physical absorption, adsorption, permeation through membranes, and chemical conversion [27]. Absorption and adsorption of acid gases is performed by aqueous solutions of alkanolamines such as are monoethanolamine (MEA), diethanolamine [28,29].

In this study, the behavior of chemical gas sensors based on multiwalled carbon nanotubes functionalized with carboxylic acids and amines such as dodecylamine and octadecyl amines are investigated in different temperatures toward natural gas contains H_2S and small amount of mercaptane. In addition, the recovery mechanisms of them are discussed.

2. Experiment

2.1. Materials

Multi-walled carbon nanotubes (MWCNT) and functionalized multi-walled carbon nanotubes were prepared in Research Institute of Petroleum Industry of Iran (RIPI) with 90–95% purity. MWCNT were obtained by enhanced CVD method over Co-Mo/MgO catalyst at a reasonably temperature of 1173 K, consisting of high purity methane (99.999%) as carbon source in a 1.5 m horizontal two pass-fixed-bed tubular (quartz) reactor placed in a 100 cm long and programmable tubular furnace [30]. The average diameters of them were varied from 10 to 20 nm and their length from 5 to 15 μm. The transmission electron microscopy (TEM) of as grown nanotube image is shown in Fig. 1. In order to obtain amido-functionalized carbon nanotubes, purification by ozonation and sonication at 60 °C with a solution of HNO_3 (65% purity) and H_2SO_4 (98% purity) (3:1, v/v) for 3 h were implemented. Therefore, one hundred milligrams of acyl-chlorinated MWNTs were added to amine compound (octadecylamine (oda) or dodecylamine (dda)). After sonication and reflux process, the black solid of functionalized MWCNT by amid groups were obtained. In Scheme 1 side wall functionalization procedures is presented briefly [31].

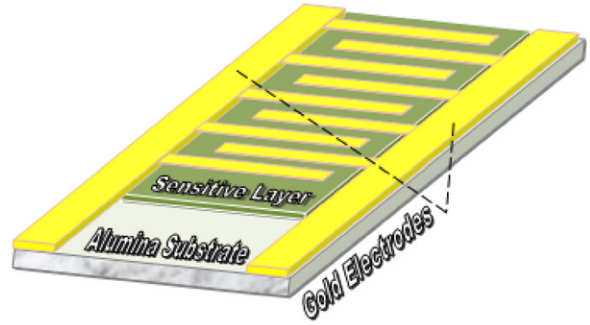

Fig. 2. A schematic top view of the gas sensor after the sensitive layer coating.

2.2. Gas sensor fabrication

The interdigitated electrodes (IDE) were fabricated through the conventional photolithographic method. Electrodes fingers are 100 μm long and have 100 μm gap size. 400 nm thicknesses of Au electrodes have been sputtered on a polished Al_2O_3 substrate with dimensions of (10 mm × 10 mm × 1 mm), at 6×10^{-6} Torr and 150 W to attain the interdigitated electrodes. Fig. 2 shows the cross-section of the fabricated sensor.

Four micro grams of each sensitive substances was dispersed and sonicated in 300 cc alcohol solvents such as 2-propanol for 2 h. Thereafter the solutions were spin coated at 500 rpm/min on Au comb electrodes and substrates. Then they were heated for 1 h in an oven at 100 °C to remove alcohols from the sensitive layers. Signal wires were connected to the electrodes by silver paste and transferred the resistance changes of sensors to data acquisition system.

2.3. Gas sensing set up and measurement

4 Manufactured sensors have installed separately in a sealed chamber with a U-shape glass tube (2.5 cm diameter and 40 cm length) as a reactor in which chemical reactions has happened. Chamber temperature has been qualified by temperature controller unit contains thermostat and K-type thermocouple. Integrated electronic circuit was designed and fabricated to calculate variable voltages by ATMEGA16 microcontroller with 10 bite ADC transformers. A DC voltage of 5.00 V was applied onto a reference resistance which was in series with the sensor. Therefore the resistance variation through the whole process can be computed. The sensors output were recorded and measured by using a self-developed software which has been prepared in the laboratory using Visual Basic programming. The experiments were accomplished on MWCNT, MWCNT-COOH, MWCNT-$CONHC_{12}H_{26}$ (MWCNT-dda) and MWCNT-$CONHC_{18}H_{37}$ (MWCNT- oda) functionalized gas sensors in different temperatures in the range of 25–80 °C and atmospheric pressure. Gas sensing detection process was initiated by N_2 injection as purge gas. N_2 flow rate was kept constant at 500 cm^3/min by a mass flow meter (GFC 110) controlling. Thereafter, natural gas (i.e. mixture of methane and 160 ppm H_2S) was injected into the chamber with 50 cm^3/min rate during each test. After exposed to sensing gas for 10 min, the sensors were exposed to the N_2 flow. The resistance variations were observed and recorded. The experimental set-up is illustrated in Fig. 3.

3. Result and discussion

3.1. Sensing characteristics

The SEM image of coated interdigitated electrodes is represented in Fig. 4a. Sensors were heat treated after coating.