Sensors and Actuators B 210 (2015) 1–8

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

High sensitive and selective flexible H_2S gas sensors based on Cu nanoparticle decorated SWCNTs

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ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form
24 November 2014
Accepted 20 December 2014
Available online 27 December 2014

Keywords:
Carbon nanotubes
Copper nanoparticles
Flexible sensors
Polyethylene terephthalate
H_2S sensing

ABSTRACT

We present sensitive flexible H_2S gas sensors operating at room temperature based on Cu-SWCNTs. SWCNTs are decorated with metallic cluster of Cu nanoparticles (NPs) by employing a reduction chemical process and are spin coated on a polyethylene terephthalate (PET) flexible substrate for achieving facile and cheap sensors. Cu-SWCNTs-based sensors show remarkable responses upon exposure to various concentrations of H_2S gas in the range of 5 ppm to 150 ppm. A fast response time and a recovery time of ~10 s and ~15 s, respectively, are obtained for 5 ppm of H_2S. Resistance modulation – without any significant degradation – is observed for bending radii larger than 4 mm. The sensors show reproducible response upon exposure to larger than 20 ppm of H_2S and bending radii larger than 7.8 mm. Ab initio simulations are performed to explore the underlying H_2S sensing mechanism of Cu-SWCNTs. In agreement with our experiments, theoretical analyses indicated that the decoration of SWCNTs with Cu atoms enhances the sensitivity of SWCNTs for H_2S gas detection.

1. Introduction

Recently, intense research efforts have been dedicated to the development of detectors and sensors for detecting ultra-low amounts of chemical agents with a relatively fast response time [1,2]. H_2S is a harmful gas to human that can cause death depending on the concentration and exposure time [3]. Hydrogen sulfide has serious erosion effects and is known to be the major source of acid rain. Hydrogen sulfide is generated in various industrial processes including natural gas processing and petroleum refining. Although several commercial devices have been developed for H_2S monitoring, they suffer from high operating temperatures, high power consumption, and high cost [4–6]. Harmful effects of H_2S, however, require the development of small, portable, fast, and sensitive gas sensors.

A single wall carbon nanotube (SWCNT) can be considered as a graphene sheet that has been rolled up into a seamless nanocylinder [7]. CNTs are being used as building blocks of advanced functional materials due to their excellent electrical properties [8–10]. SWCNTs have been widely used as the channel materials for field effect transistors (FETs) [11–13], electrochemical sensors [14–17], gas sensors [18–22], and biosensors [23–25]. The sensitivity of CNTs to the surface charge transfer is the key advantage of their applications as sensing elements [26]. Because of low level selectivity and sensitivity of pristine SWCNTs to chemical gases, various approaches have been used for functionalizing SWCNTs by polymers [27], enzymes [28] and metallic clusters [29].

In recent years, flexible sensors have been extensively used for direct attachment to the body skin for wearable smart and portable consumer device applications [30,31]. Flexible sensors can be adopted for a wide range of applications due to their light weight, low cost, and mechanical flexibility [32–34]. Excellent mechanical properties of CNTs render them as prominent candidates for flexible devices. Recent studies show that CNTs can be easily assembled on flexible substrates using spray and plasma treatments [35]. Therefore, flexible sensors with CNTs are very promising for gas sensing application [36–38]. In this study, we present relatively fast and flexible sensors, employing SWCNTs decorated with Cu NPs for the detection of H_2S. SWCNTs-based sensors are fabricated on a polyethylene terephthalate (PET) substrate which has a high degree of flexibility and transparency.

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http://dx.doi.org/10.1016/j.snb.2014.12.086
0925-4005/

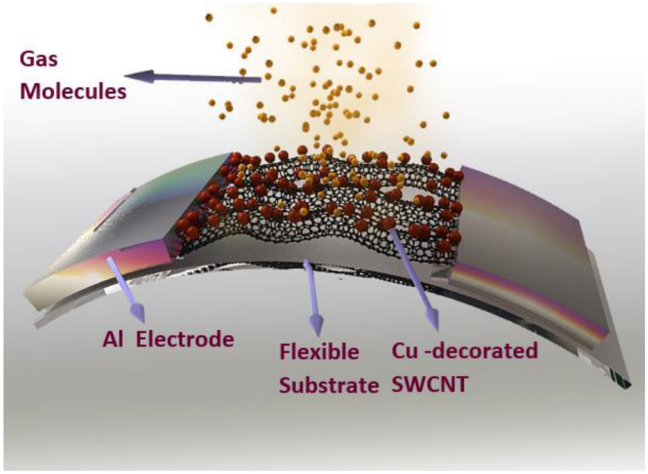

Fig. 1. The schematic of the fabricated SWCNT-based gas sensors on a flexible substrate.

2. Experiments

2.1. Materials and methods

SWCNTs (with outer diameters of ~1–2 nm, lengths of ~30 μm, purity 90%, supplied by Parsis Co. Iran) are used as building blocks of the sensitive film. SWCNTs sidewalls are functionalized by carboxyl groups using acid treatment process: 50 mg of pristine SWCNTs are dispersed in a solution of H_2SO_4:HNO_3 (1:3) followed by sonication at 60 °C for 2 h. This process leads to the formation of active sites that are negatively charged which in turn facilitate chemical bonds. Functionalized SWCNTs (F-SWCNTs) are filtered and washed with DI water several times until a neutral PH is achieved. The F-SWCNTs are decorated by Cu NPs by a chemical reduction process: 50 mg F-SWCNTs are added in DI water and stirred for 15 min. Then 20 mg $CuSO_4$ are added in solution consequently and stirred at 80 °C for 30 min. Following this process Cu ions (in the shape of Cu^+ and Cu^{2+}), as described by Pike et al. [39], are reduced and deposited on the functionalized sites at SWCNT's walls which are negatively charged. The final nanomaterial is filtered and dried in vacuum oven at 60 °C for 8 h.

Aluminum interdigital transducers (IDTs) are used as contacts for Cu decorated SWCNTs (Cu-SWCNTs) based gas sensors. In order to fabricate IDTs on flexible substrates, micro-scale patterning on PET films can be employed: a layer of photoresist is patterned on the substrate with conventional photolithography process, 200 nm of Al layer (deposited by DC magnetron sputtering system, Nanosctructured Coating Co., Iran) is then coated on the substrate followed by a lift-off process by the immersion of the flexible substrate in sonicated acetone. Finally, Cu-SWCNTs are spin-coated onto the patterned substrate and then annealed in a vacuum oven at 80 °C for 30 min. Fig. 1 shows the schematic structure of a flexible sensor with assembled Cu-SWCNTs.

2.2. Characterization

The surface morphology of Cu-SWCNTs is characterized using field emission scanning electron microscope (FE-SEM, Hitachi S4160). We have performed Energy Dispersive Spectroscopy (EDS) analysis on the Cu NP decorated SWCNTs to indicate the Cu loading on the final sensitive film. For sensitivity assessing of the fabricated sensors, they are loaded in an aluminum chamber (150 ml volume) and they are outgassed in the vicinity of argon gas for 1 min. Argon is used as a dilution gas for removing the effect of humidity and oxygen on the sensing mechanism of the fabricated sensors. The required concentrations of H_2S and argon are measured by mass flow controllers. The time dependent electrical resistance is measured at various gas concentrations from 5 ppm to 150 ppm, using a computer-based data acquisition system. For the measurements a fix bias voltage of 1 V is applied to Al electrodes. For the recovering process, after steady state, each sensor is exposed to dry argon to attain 90% of the total resistance change. Before each measurement, the outgassing procedure is carried out by holding the sensors in a constant flow of argon and the initial resistance is registered. To evaluate the selectivity toward various gases, the devices are exposed to acetone, ethanol, and H_2. The effects of bending radius on the flexible sensors are analyzed at bending radii larger than 4 mm. Influence of the humid condition on the response characteristics of the fabricated sensors has been investigated under 40% relative humid ambient at room temperature.

2.3. Computational method

To understand the adsorption mechanism of H_2S gas in Cu-SWCNTs, ab initio studies are performed, employing the SIESTA code [40]. Two (10,0) carbon chains are selected as the unit cell. The structure of the isolated (10,0) SWCNT, Cu-SWCNT, H_2S and their complex system (H_2S/Cu-SWCNTs) are optimized by GGA pseudo potential approximation. To optimize the geometry of the atoms, the minimum force on each atom is set to 0.05 eV/Å. The mesh cut-off energy is set to 150 Ry. An unrestricted $1 \times 1 \times 4$ Monkhorst-Pack grid for k-point sampling of the Brillouin zone is used [41]. Three different initial configurations of Cu-SWCNTs are considered for the optimization processes. Finally, the adsorption of a single H_2S molecule on the Cu-SWCNTs is considered. One of the main focuses in this calculation is to obtain the binding energies and electronic properties of the Cu-SWCNT due to H_2S gas adsorption. The binding energy of H_2S molecule adsorption on the Cu-SWCNT (E_b) is calculated as follows:

$$E_b = E(H_2S/\text{Cu-SWCNT}) - E(\text{Cu-SWCNT}) - E(H_2S), \quad (1)$$

where $E(H_2S/\text{Cu-SWCNT})$ is the total energy of the H_2S adsorbed on the Cu-SWCNT, E(Cu-SWCNT) is the total energy of the Cu-SWCNT, and $E(H_2S)$ is the total energy of the isolated H_2S molecule.

3. Results and discussions

3.1. Structural study and EDS analysis

Fabricated devices on a PET substrate are shown in Fig. 2a. The photograph clearly shows that the substrate with Al electrodes can be easily bent. The electrode fingers have a height of 5000 μm and a gap size of 200 μm. Spin coated thin films of Cu-SWCNTs show strong adherence on the substrate. As shown in Fig. 2b pristine SWCNTs are dispersed as bare bundles and Fig. 2c illustrates that SWCNT bundles are successfully decorated with Cu NPs. The dense decoration of Cu NPs on the sidewalls of SWCNTs leads to increased sensitivity of the sensors. Fig. 2c depicts densely linked metallic cluster of Cu nanoparticles on the CNT sidewalls.

The elemental composition of SWCNTs decorated with metallic cluster of Cu NPs has been investigated by EDS analysis. Fig. 2d shows the elemental ratio of Cu, O and C peaks. The oxygen peak can be attributed to functionalized surface of the SWCNT after acid treatment and also to the presence of the CuO composition at the sidewalls of the SWCNT. The qualitative and quantitative analyses have been used to find out what elements in which relativity exists in our prepared sensitive material. The EDS analysis represents the Cu/C peak ratio of 0.25, which is consistent with decomposition of $CuSO_4$ and reduction of Cu ions into metallic nanocluster. By adjusting the concentration of $CuSO_4$ in the starting solution, the Cu loading in the final Cu-SWCNTs sensitive material can be controlled.