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Study of simultaneous reversible and irreversible adsorption on single-walled carbon nanotube gas sensor

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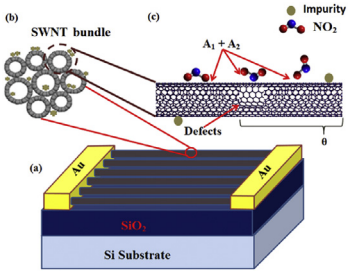
HIGHLIGHTS

- An aligned micro network of SWCNT is fabricated by dielectrophoresis method for gas sensing study.
- NO_2 ranging from 0.5 to 10 ppm is exposed to gas sensor; the gas sensor follows the dose effect for exposed concentration.
- A model is developed to explain the response of the SWCNT gas sensor.
- In this model, it is assumed that reversible and irreversible adsorption take place simultaneously on the sensor surface.
- This model explains the experimental data reasonably well for all exposed concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper represents the adsorption kinetics of NO_2 on single-walled carbon nanotube (SWCNT) gas sensor. The gas sensor is exposed to different concentrations of NO_2 (0.5–10 ppm) for gas sensing study. To study the adsorption kinetics of analyte over SWCNT surface, an adsorption model is developed using site balance equation and mass action law. In this model, we consider the availability of reversible and irreversible adsorption sites, where analyte is adsorbed simultaneously with different rates. This model explains the response curves reasonably well and it is further used to extract the irreversible and reversible rate of reaction for different NO_2 concentration exposed to gas sensor. The irreversible and reversible rate of reaction for SWCNT lies in the range 1.51×10^{-5} to 3.17×10^{-5} $ppm^{-1}s^{-1}$ and 1.68×10^{-2} to 9.8×10^{-4} $ppm^{-1}s^{-1}$ for different gas concentration exposed. The activation energy of reversible site lies in the range 0.6–0.8 eV, which lies within the reported range.

1. Introduction

Single-walled carbon nanotube (SWCNT) with inherent nano scale features has great potential for becoming ideal components for the next generation gas sensor technology. SWCNT gas sensors

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have received interest because of their unique properties such as faster response, higher sensitivity and selectivity, lower operating temperature, and the ability to detect different types of gases [1–6].

The adsorption is a surface phenomenon in which analyte molecules accumulates on the gas sensor surface and experiences an intermolecular interaction force which leads to change in the surface energy [7]. SWCNTs form bundle by adhering to each other due to strong vander wall interaction and high aspect ratio [8–10]. These bundles contain SWCNTs of different diameter distribution [11,12]. There are distinct sites available on these bundles for analyte to be adsorbed due to heterogeneous nature of SWCNT bundle as adsorbent [13,14]. The gas adsorption on these sites depends on diameter of neighbour tubes, size of gas molecules, specific structure and total specific area of the SWCNT bundle, binding energy as well as availability of the sites [15]. The gas adsorption processes can be categorized as reversible (physisorption) [16] or irreversible (chemisorption) [17–19] or may be combination of both [20,21] which depends on the type of interaction [22–25]. Both mechanisms can play an important role in gas sensing [26]. The defect sites present on SWCNT serve as low energy sites as well as nucleation sites at higher concentration and contribute to gas sensor response [15,27].

It has been reported that SWCNT sensor is sensitive to various gas/vapors and shows reversible response to H_2, ethanol and 1-propanol [16,28], and irreversible response to NO_2, NH_3 and O_2 [1,17–19]. It is often seen that SWCNT based gas sensor shows partial recovery and a significant drift in base resistance is observed after multiple exposures [1,29,30]. This type of gas sensor needs extra energy in the form of UV light, or heat or gate voltage for forced recovery to baseline [29,31–33].

In earlier reported papers, adsorption of analyte on the gas sensor surface has been analysed either in the light of reversible or irreversible process [34,35]. The model assumed uniform adsorption sites on gas sensor surface and failed to explain the adsorption curve [34–37]. To explain adsorption curve, they assumed two types of adsorption sites to be available on gas sensor surface, and the sum of two exponential terms has been taken to fit the response curves. There is no mathematical model taking under consideration the description of how adsorption takes place on these sites and how these sites are related to each other.

In this work, to study the adsorption kinetics of analyte on the gas sensor surface, we assumed that adsorption of analyte takes place simultaneously on reversible and irreversible sites of single walled carbon nanotube. We have analysed the simultaneous reversible and irreversible adsorption on gas sensor surface by establishing a general model. The reversible and irreversible rate of reaction for exposed NO_2 to gas sensor has also been deduced using the model. This model is successfully used for the analysis of experimental data of the response curve.

2. Experimental

SWCNT micro resistive (SWCNT-μR) network was prepared using Arc discharge single-walled carbon nanotube powder procured from Carbon Solution Inc. To fabricate SWCNT-μR, SWCNT suspension was prepared by dispersing 0.2 mg of SWCNT in 100 ml of DMF and ultrasonicated for 2 h. A small piece of the diced die having pre-patterned micro-electrodes of gold/germanium on the SiO_2/Si substrate was mounted on the transistor outline (TO) header of 8 pins. The die had 3 electrodes with 4, 6, 4 fingers and having gap 10 μm each. The contacts were made using gold wire. SWCNT dispersion was dropped using micropipette of 1 μl droplet between the electrode gaps. For alignment of SWCNT, AC field of 1 MHz and peak-to-peak voltage of $10V_{pp}$ was applied for 5 s. The typical resistance between the three electrodes was 17.2162 and 930 kΩ. The fabricated gas sensor was placed inside a gas cell under constant flow of N_2. The gas concentration was generated by diluting NO_2 with N_2. Sensing measurement was carried at room temperature. The resistance measurement of sensor was done by Fluke 289 DMM.

The surface morphology of the SWCNT is observed by field emission scanning microscope (FE-SEM) Ziess Auriga SUPRA 55 and TEM observation by EM instrument of FEI TecnaiG^2. The Raman characterization is performed on 800SE HORIBA Scientific Raman spectroscopy.

3. Results and discussion

3.1. Gas sensor characterization

The structural properties of SWCNT are evaluated with Raman spectrum shown in the Fig. 1a. The radial breath mode (RBM) of SWCNT lies between 139 and 202 cm^{-1}, G with G^- and G^+ lies at about 1569 $cm^{-1}$and 1590 cm^{-1}, and G′ peak lies at 2670 cm^{-1} [38,39]. The intensity of disorder induced D peak is very small and lies at about 1342 $cm^{-1}$and the ratio between I_G/I_D is 76 indicating some defect SWCNTs [30]. The diameter of SWCNT is calculated from the RBM peak using the formula $\omega_{rbm} = A_1/d_t + A_2$, where d_t is the diameter of SWCNT and A_1, A_2 are experimental constant with values 234 cm^{-1} and 10 $cm^{-1}$for SWCNT bundles [38,40]. The diameter of SWCNT lies in the range of 1.2–1.8 nm. The SWCNTs aligned between the electrodes is shown in Fig. 1b. The SWCNT are in bundle form having average diameter 20–30 nm. The SWCNT bundles lie on the top of the substrate and are accessible to the guest molecules.

The structure of the SWCNT is examined from the TEM image, as shown in Fig. 1c. The inset Fig. 1c shows that SWCNTs tube walls are well connected to each other in bundle form and diameter of these bundle lies in the range 8–25 nm. Two dark parallel lines represent the individual SWCNT [41]. The average diameter of the individual SWCNT observed in the TEM image is approximately of 1.6 nm. The black spots along the sidewall of SWCNTs bundles represents the presence of a very small amount of amorphous carbon as also confirmed from G/D band intensity ratio.

3.2. Gas sensing

The gas sensor of resistance 17.2 kΩ is used for gas sensing study. The gas sensor baseline noise depends on the resistance of the gas sensor lesser the resistance smaller the noise [42,43]. SWCNT gas sensor was pretreated under N_2 gas flow before exposing the different concentration of analyte to ensure that base line drift is less than 0.2% in 5 min. All experiments are carried out at ambient conditions. SWCNT gas sensor is exposed to different NO_2 concentration (0.5–10 ppm) with the next concentration exposed after recovery of sample to baseline in the presence of UV and N_2 [29,44]. Recovery of gas sensor is not shown here. When the gas sensor is exposed to NO_2, the conductance of SWCNT gas sensor increases due to adsorption of the NO_2 on the SWCNT sites [1,45]. The response of sensor increases with increase in the concentration of gas exposed. Fig. 2a shows a typical conductance response for NO_2. The SWCNT gas sensor is unable to recover completely even after 12 h [1,30] without forced recovery, which indicates that the irreversible type of adsorption is taking place on gas sensor surface. To confirm the type of adsorption of NO_2 on SWCNT surface, dose vs response graph is plotted as shown in Fig. 2b. The response curve of 10, 5, 2 and 0.5 ppm completely overlay each other. There is similar change in the response of gas sensor when it is exposed with same dose (ppm*min). This indicates there is significant amount of adsorption occurring on the surface of gas sensor which is