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Functionalized Multi-Walled Carbon Nanotubes for Nitrogen Sensor

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Abstract: *Multiwalled Carbon Nanotubes (MWCNTs) produced by the arc discharge method are chemically functionalized with acid mixture. The functionalization of MWCNTs was confirmed by simple characterization techniques. This revealed that carboxylic group introduced, without disrupting main structure of MWCNTs. The gas sensing performance of the functionalized MWCNTs towards NO_2 is studied. The highest sensitivity of 26.88 % for 100 ppm of NO_2 at 27°C is observed towards functionalized MWCNTs.*
Keywords: *Carbon nanotubes, Functionalization, Reflux, Response time, Carboxylation*

I. Introduction

CNTs are sheets of carbon atoms arranged in hexagons that curl into a tube [1] possessing unique electrical and electronic properties. The extremely high surface-to-volume ratio and hollow structure of CNTs is ideal for the adsorption of gas molecules [2]. Many researchers [3-5] have shown that as produced CNTs has the tendency to exist in bundles rather than as individual tubes, because of strong Vander Waals interactions, leading to insolubility in most organic media, and therefore limiting the range of applications. A common technique to improve dispersion and achieve optimum utilization of CNTs is its chemical functionalization [6, 7]. The development of highly sensitive chemical sensors is an attractive area of research because of their widespread applications in the industry, agriculture, environment, biomedicine and pharmaceutics. The principles of CNT- gas sensors for the detection of different gases are based on changes in electrical properties induced by charge transfer with the gas molecules [8]. A study of a pristine CNT-based sensor reports slow and incomplete recovery [9, 10]. To overcome these limitations, improvement of interfacial interaction can be achieved by the functionalization of CNTs. The polar groups on the nanotubes surface increase the adsorption affinity of the electron-donor or acceptor gases and enhance their sensing performance [8].

II. Experimental

100 mg pristine MWCNTs were refluxed with of H_2SO_4 + HNO_3 (3:1) at 55 °C for 11 h. Then reaction mixture was stirred at 40 °C for 12 h and diluted three times with distilled water, filtered using centrifuge machine having 8,000 rpm. The process of centrifugation and washing off with distilled water repeated till neutral pH. Then the sample dried in vacuum oven at 50 °C for 24 h gives carboxylated MWCNTs (MWCNT-COOH). This leads to opening the caps of MWCNTs [11]. A certain amount of MWCNT-COOH powder was suspended in 20 ml distilled water in beaker by ultrasonic stirring for 20 min. After well dispersion in distilled water thin films made on glass substrate using dip coating method. Then this film was tested upon exposed to NO_2 gas. The sensing properties of the film were studied at different temperatures and at different concentrations.

III. Reaction Mechanism

The possible reaction takes place during Carboxylation of CNTs is given in "equation 1". Fig.1 describes gas sensing mechanism of functionalized CNTs towards NO_2 gas.

$$\mathrm{MWCNT} + \mathrm{H_2SO_4 : HNO_3} \rightarrow \quad \mathrm{MWCNT - COOH} + \mathrm{H_2O} + \mathrm{SO_2} + 2\,\mathrm{NO_2} \qquad (1)$$

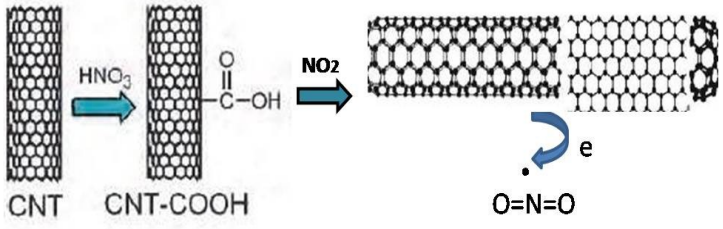

Fig.1: Reaction mechanism takes place during functionalization and sensing response

III. Results and Discussion

X-Ray Diffraction (XRD) Studies

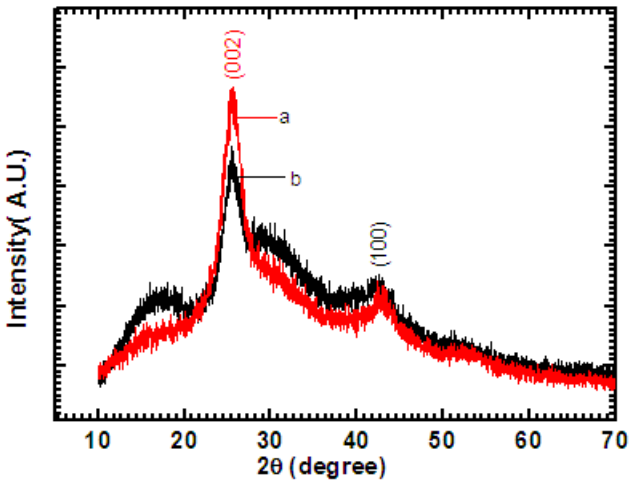

Fig.2: XRD spectra of the a) pristine MWCNT b) MWCNT-COOH

XRD patterns of the pristine MWCNT and MWCNTs-COOH, samples are shown in Fig. 2. The pristine MWCNT samples revealed the presence of two peaks at 25.70° and 42.43° corresponds to (002) and (100) planes of the carbon atoms respectively with interlayer spacing (34 nm) [12]. There is no drastic change in the position of characteristic peaks of pristine MWCNTs and MWCNT-COOH was observed, which suggests that MWCNTs are retained with their original structure after functionalization.

Fourier Transform Infrared (FT-IR) Studies

FT-IR spectra in the range 4000–400 cm^{-1} were recorded in order to investigate the nature of the chemical bonds formed. The FT-IR spectra of the pristine and functionalized MWCNTs are shown in Fig. 3

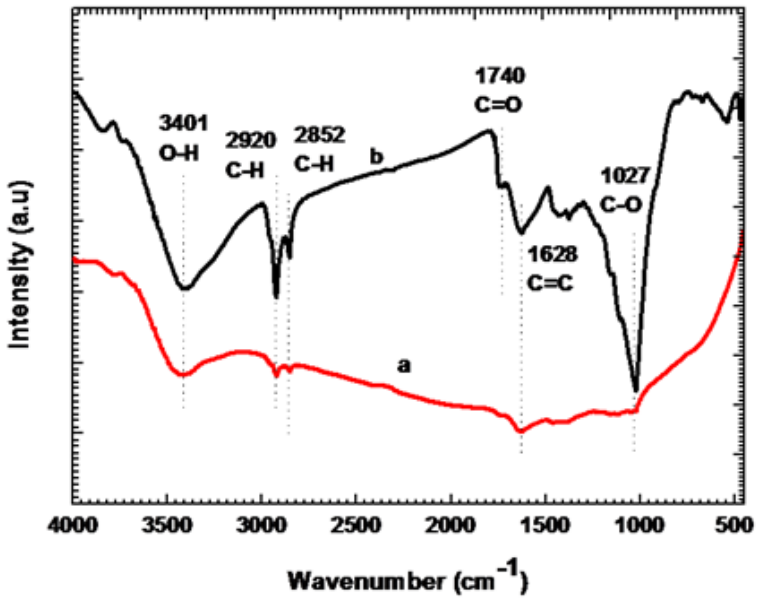

Fig. 3: FT-IR spectra of the (a) pristine MWCNTs and (b) MWCNT-COOH powder samples

Fig. 3(b) shows characteristic peaks of MWNT-COOH at 1027cm^{-1} (C-O), 1628 cm^{-1}(C=C), 1740 cm^{-1} (C=O), and 3401 cm^{-1} (-OH). As compared with the FT-IR spectrum of pristine MWCNTs (Fig. 3 (a)), the peaks at ≃1740 and 1027 cm^{-1} in Fig. 3(b) were from the stretching vibration of C=O and –C-O groups in the carboxyl group (-COOH), respectively [13,14].

Scanning Electron Microscopy (SEM) Studies

SEM is used to observe the morphologies of the MWCNTs. In Fig. 4(a) tubes of pristine MWCNTs can be clearly seen. Whereas the amorphous carbon layer is deposited on the surface of MWCNT-COOH ((Fig. 4

(b)). Compared with pristine MWCNTs, the functionalized MWCNTs are shorter in length. The acid treatment can fragment the MWCNTs [15]. Many entangled clusters of functionalized MWCNTs are observed. Broken or damaged MWCNTs are more amenable to functionalization than pristine CNTs, due to the higher concentration of defects.

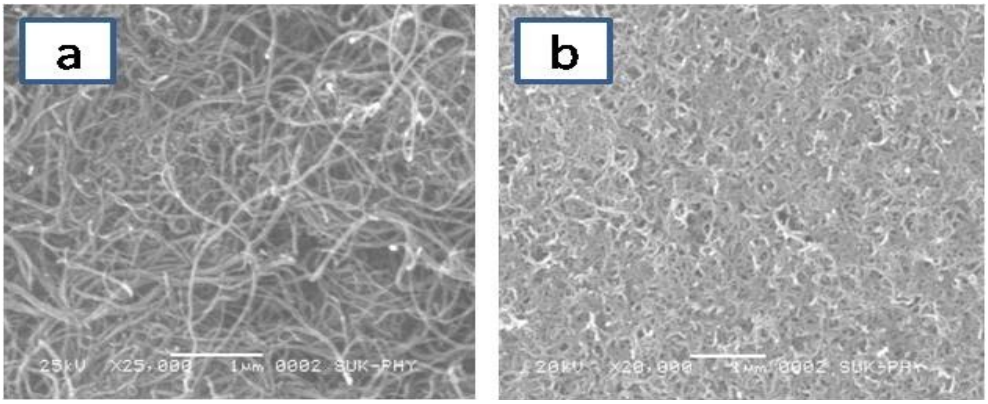

Fig. 4: SEM images of the (a) pristine MWCNT (b) MWCNT-COOH

Gas sensing Study

In present study, the sensing properties of MWCNT-COOH was studied at different temperatures from 50 °C to 225 °C and at different concentrations (50, 100 and 200 ppm) toward NO_2 under continuous flow of NO_2 gas. The response (S) of the sensor is expressed as the ratio of the change in resistance (ΔR) upon exposure to absorbed vapor to the resistance (R_A) of the sample in the air [16] as shown by "equation 2".

$$S = \frac{\Delta R}{R_A} X\ 100\ \% \qquad (2)$$

Where ΔR is the resistance difference between R_G and R_A, and R_G denote the resistance of the sample measured in the presence of absorbed vapor. Fig. 5 demonstrates the dynamic response of MWCNT-COOH sensor on exposure to NO_2 at different vapour concentration, viz., 50,100 and 200 ppm. Table1 summarizes response time, recovery time and sensitivity of MWCNT-COOH towards NO_2 at different temperatures and concentrations.

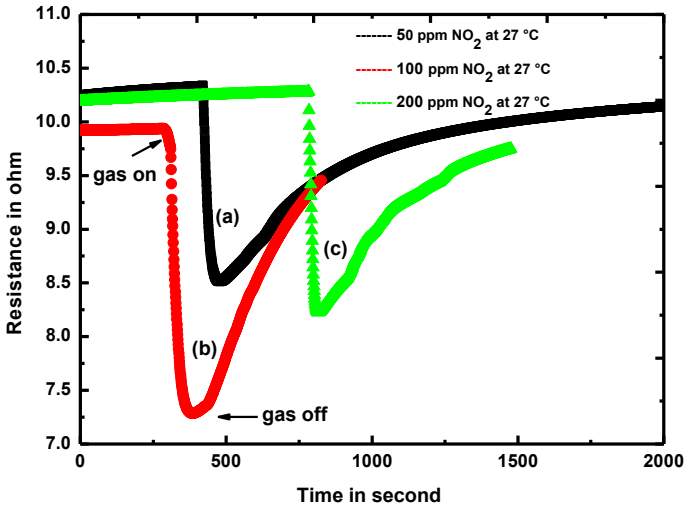

Fig. 5: Sensing response of the MWCNT-COOH at (a) 50 ppm (b) 100 ppm (c) 200 ppm

Table1. Sensing response of MWCNT-COOH towards NO_2 at different temperatures

Temperature (°C)	Gas concentration (ppm)	Response time (sec)	Recovery Time (sec)	Response (%)
50	50	565	158	13.69
75	100	351	3	10.27
100	100	464	1	9.06
150	100	114	113	16.25
200	100	54	18	11.62
225	100	48	2	9.24
room	50	265	265	17.98
room	**100**	**230**	**288**	**26.88**
room	200	240	251	20.25

IV. Conclusion

We reported here a synthesis of carboxylated MWCNTs using a chemical method. Treatment with strong acid mixture results in formation of carboxyl groups. The XRD spectra shows that the intensity of the (002) peaks decreases monotonically as MWCNTs gets functionalized. The FT-IR spectra confirm the presence of –COOH, functional group. SEM image shows that acid-treatments shorten the length of MWNTs. MWCNT-COOH exhibited good response towards NO_2 at 27°C for 100 ppm.

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