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Enhancement in the performance of multi-walled carbon nanotube: Poly(methylmethacrylate) composite thin film ethanol sensors through appropriate nanotube functionalization

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ABSTRACT

We report for the first time, development of an efficient ethanol sensor using mild functionalized multiwalled carbon nanotubes (MWCNTs). A unique technique to functionalize MWCNT is reported to enhance the performance of the ethanol sensor based on it. The conventional functionalization techniques tend to damage physical structure of carbon nanotubes (CNTs) to a large extent and convert most of their sp^2 bonds into sp^3 bonded carbon atoms. This results in reduction of the available adsorption sites for ethanol vapors on the CNT surface and hence deteriorates the sensitivity. In this work, the functionalization of nanotubes is achieved through direct cycloaddition to π electrons of the CNT that does not hamper the physical structure of the nanotube. High resolution transmission electron microscopy (HRTEM) and Raman spectroscopy studies were employed to confirm the appropriate functionalization for better performance of the sensor. Electrical transport properties of the composites were also studied to understand the quality of the established CNT network. Out of the other functionalization technique, Diels Alder cyclo addition reaction based composite sensor was found to exhibit excellent performance and has an edge over the other reported CNT based sensor.

1. Introduction

In the past few years [1–6], numerous efforts have been directed towards improving the performance of polymer: multiwalled carbon nanotube (MWCNT) composite sensors for detection of ethanol. This is due to their enhanced characteristics (such as sensitivity, selectivity and stability at room temperature) as compared to their conventional alternatives based on metal oxides, polymers, or even pristine carbon nanotubes (CNTs) [6–9]. These polymer composites fully exploit the fascinating properties of CNTs viz light weight, high mechanical strength, large surface area, high conductivity and ability to quickly respond to the local environmental conditions

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Table 1
A Comparative table of available ethanol sensor.

Sensing material	Fabrication method	Response/recovery time (seconds)	Response ($\Delta R/R_0$)	Reference
PMMA–CNT	Spray layer by layer	Not mentioned	4.65	[3]
Poly(diallyldimethyl-ammonium chloride/sodium deoxycholate–CNT)	Electrostatic layer by layer assembly	$15\times10^3/12\times10^3$	0.45	[2]
Oxidized MWCNTs	Vacuum filtration method	250/300	32	[5]
MWCNTs/Polyethylene oxide	Solution blending	60/60	3	[6]
PMMA–CNT	Spray layer by layer	120/140	11.9	[4]

[10–12]. The polymer composites can be easily shaped, withstand high service temperatures and are mechanically resistant, provided that the CNTs are adequately dispersed within the polymer matrix [2]. Further, the thin film structures of the composite can be embedded in or near the source of organic compounds, yielding the possibility of early detection. For this purpose, composite tapes can be fixed on pipes or fuel tanks to detect any leakage. Food grade packaging materials can also be coated with these composite films to enhance their shelf life by absorbing any unwanted vapor in the surroundings [13].

The work done by various researchers in this area is listed in Table 1. On comparing these results, it can be observed that there is always a tradeoff among the sensitivity, response and recovery time. Among these Razak et al. [6] reported the lowest response time ($\sim$60 s) where low cost solution blending technique was used to prepare the composite sensor. However, the response ($\Delta R/R_0$) that they could obtain was quite low. Here $\Delta R=R-R_0$, R_0 and R are initial resistance and maximum steady state resistance respectively. None of the groups till date could produce an ethanol sensor satisfying all three requirements of being fast, highly sensitive and cost effective.

Therefore, there is a need of in depth study of the factors that control the performance of the sensor. The rigorous literature survey suggests that the important parameters on which the sensor performance depends are doping content of CNTs in the composite, degree of mixing of the nanotubes in the polymer matrix, surface chemistry of the nanotubes and characteristics of the polymer matrix [9,14–15].

In our previous studies [9], we have worked on the first parameter i.e. doping content of CNTs in the polymer matrix. We have shown that the sensor exhibits excellent performance, if the doping content of CNTs in the polymer matrix is just above the percolation threshold. This was explained with the help of percolation theory [14,16–18]. In the present study, we have investigated the effect of: (i) degree of mixing i.e. homogeneous dispersion of CNTs in the polymer matrix [19] and (ii) surface chemistry of nanotubes i.e. concentration of sp^2 bonded and sp^3 bonded carbon atoms on the nanotube surface. Both of these factors can be improved by functionalization of CNTs. However, conventional functionalization techniques, reported by various researchers [20–25], do physical damage to the CNTs in the form of sidewall destruction and length shortening, with impairment of the mechanical properties. Therefore, there is an urgent requirement of a suitable functionalization technique that does not significantly hamper the nanotube structure.

We have prepared the composite of MWCNT:PMMA (poly (methyl methacrylate) by using a simple and inexpensive solution processing technique. We have employed MWCNTs, which were functionalized under three different mild conditions. It involves direct cycloaddition to the π-electrons of the CNTs, which do not induce CNT shortening and cause little damage to the CNT surface [26,27]. To estimate the degree of mixing of the nanotubes, high resolution transmission electron microscopy (HRTEM) measurements were done and surface chemistry of the CNTs was studied by Raman spectroscopy. Further, the electrical conductivity of the composite was studied to calculate the percolation limit of each composite. Finally, the ethanol sensor was fabricated and the effect of functionalization on the sensing characteristics was examined.

2. Experimental details

The polymer PMMA and solvent nitro methane were commercially procured from Sigma Aldrich, USA. The MWCNTs (Trade name NC 7000 from Nanocyl™ produced by catalytic carbon vapor deposition) were functionalized using the following methods:

a) 1, 3-dipolar cycloaddition (DCA) reaction using *N*-benzyloxycarbonylglycine (Z-Gly-OH) and paraformaldehyde, under solvent-free one pot conditions: an ethanolic suspension of Z-Gly-OH and paraformaldehyde (1:5 M ratio) was prepared and CNTs were added into this suspension. This solution was then gently heated until the solvent was completely removed resulting in deposition of thin layer of Z-Gly-OH and paraformaldehyde on the CNT surface. This mixture was then heated at 250 °C for 3 h in round bottom flask. The so obtained nanotubes were washed several times with ethanol, filtered and dried as described in our earlier work [26] These functionalized nanotubes were denoted as sample B while sample A corresponds to the as-received NC7000.
b) It involves treatment of the nanotubes obtained after DCA reaction with polar and non-polar solvents to wash away polar and non-polar contaminants in the order ethanol, n-hexane, acetone and ethanol. These functionalized nanotubes were denoted as sample C.