Materials Research Bulletin 78 (2016) 53–57

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Resistive sensing of gaseous nitrogen dioxide using a dispersion of single-walled carbon nanotubes in an ionic liquid

Prabhash Mishra[a,b], V.S. Pavelyev[b], Rajan Patel[c], S.S. Islam[a,*]

[a] Solidstate Electronics Research Laboratory (SERL), Faculty of Engineering and Technology, Jamia Millia Islamia, Jamia Nagar, New Delhi 110025, India
[b] Department of Nanoengineering, Samara State Aerospace University, 443086 Samara, Russia
[c] Center for Interdisciplinary Research in Basic Sciences (CIRBSc), Jamia Millia Islamia, Jamia Nagar, New Delhi 110025, India

ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form 15 January 2016
Accepted 11 February 2016
Available online 15 February 2016

Keyword:
A. Nanostructures
B. Chemical synthesis
C. Electron microscopy
C. Raman spectroscopy
D. Surface properties

ABSTRACT

Single-walled carbon nanotubes (SWCNTs) were dispersed in an imidazolium-based ionic liquid (IL) and investigated in terms of structural quality, surface functionalization and inter-CNT force. Analysis by field emission electron microscopy and transmission electron microscopy shows the IL layer to coat the SWNTs, and FTIR and Raman spectroscopy confirm strong binding of the ILs to the SWNTs. Two kinds of resistive sensors were fabricated, one by drop casting of IL-wrapped SWCNTs, the other by conventional dispersion of SWCNTs. Good response and recovery to NO_2 is achieved with the IL-wrapped SWCNTs material upon UV-light exposure, which is needed because decrease the desorption energy barrier to increase the gas molecule desorption. NO_2 can be detected in the 1–20 ppm concentration range. The sensor is not interfered by humidity due to the hydrophobic tail of PF6 (ionic liquid) that makes our sensor highly resistant to moisture.

1. Introduction

SWCNTs are remarkable technological and multifunctional nanomaterial useful for numerous potential applications[1–3]. Because of their π-electronic surface structure SWCNTs provide excellent electrical, optical and mechanical properties [4–7]. However, the major drawbacks of SWCNTs lie in its process ability and poor solubility in both aqueous and non-aqueous solvents [8]. In addition, SWCNTs, in general, get heavily entangled with each other due to their strong van der Waals attraction among tubes and exist as ropes and bundles [9] which limits greatly their application in many fields [10]. To solve this inherent problem, many approaches have been attempted for instance, using surfactant induced dispersion [11,12], sidewall functionalization [13,14], polymer and DNA wrapping [15,16], chemical modification through π-stacking with atomic molecules [17]. These treatments are harsh, disruptive and moderate dispersion is possible for SWCNTs used in a small scale. For large scale application, a much simpler and more efficient method is needed for SWCNTs dispersion in higher concentration with lesser degree of defects and surface damage.

IL is a series of organic molten salts whose unique properties can easily be tailored by combining one of the ions [18]. Currently, ILs have attracted much attention as a replacement for traditional organic solvents as they possess many attractive properties such as ionic conductivity, low volatility, high chemical and thermal stability, and wide electrochemical windows [19]. Due to these unique properties, they have been widely used as environmentally benign solvents in many fields, such as chemical reaction, catalysis, electrochemistry and liquid/liquid extraction [20]. The practical use of ILs in electronic device applications comprising actuators [21], supercapacitors [22], electrochromic devices [23], and solar cells [24] with significant improvements in lifetimes and device performance. Some research works have been carried out in the field of electrochemical sensors to detect gaseous, inorganic/organic vapors, and biological analytes [19]. But no article is found in the literature on solid state sensor comprising ionic liquid and SWCNTs for toxic gas sensing application.

Good dispersion leads to increase in surface area of SWCNTs. Since sensing is a surface activity phenomenon, therefore, the use of ILs as dispersant and its application as sensor is a good concept. This should make the improvement in sensing response, sensitivity, and resolution and detection range. The increase in surface area of SWCNTs by using ILs as dispersant has tempted the researchers in the current years to go for SWCNTs based sensor devices [25] and the reports are available on the efficient dispersion of SWCNTs in IL as well [26]. Some research groups have reported the IL

* Corresponding author.
E-mail address: sislam@jmi.ac.in (S.S. Islam).

http://dx.doi.org/10.1016/j.materresbull.2016.02.016
0025-5408/

modified nanotubes dispersed in polyurethane [27], ionic polymers and poly(vinylidene fluoride)(PVDF) [28]. Efficient dispersion of SWCNTs in the imidazoliumbased room-temperature IL is also reported [29]. Although ILs have been used to prepare homogeneous SWCNT dispersion, any investigation as well as comparative study to find the efficacy of it as dispersing agent vis-à-vis the other dispersing agents and its effect on the toxic gas sensing behavior by a SWCNT-based solid state sensor have been done yet.

We have synthesized [C6-mim] PF6 as reported by Caitlin L. Williamson and co-workers [30] and a homogeneous dispersion solution of SWCNT based on IL-modified SWCNT and N,N-Dimethylformide (DMF). The focus has been placed on the functions of [C6-mim] PF6-wrapped SWCNTs in the prepared dispersion solution and its impact on sensor parameters. Electron microscopy, Raman Spectroscopy, FTIR spectroscopy and UV–vis spectroscopy were used to characterize the IL wrapped SWCNT and its dispersion in DMF. Resistive sensors were prepared by drop-cast method using IL-modified SWCNTs as sensing element. Excellent response and sensitivity have been observed at 1 ppm NO_2 concentration as compared to sensors where traditional dispersion agent is used. NO_2 recovery is a serious issue and 100% recovery has been brought from several hours to few minutes using UV-light excitation.

2. Experimental

2.1. Synthesis of ionic liquid

Preparation of ionic liquid comprises certain steps where the first step constitutes heating an equimolar amount of 1-methylimidazole and 1-bromohexane at reflux for 20 min followed by cooling to room temperature. Then added water and Potassium hexafluorophosphate (KPF_6) and swirled at room temperature for 10–15 min. In the next step, ionic liquid were isolated by dichloromethane extraction and distillation.

During reaction between 1-methylimidazole and 1-bromobutane, potassium bromide is obtained as a byproduct in the form of impurity. These byproducts alter the physical properties. Excess of halide based by-products also lead to hindrance in the final product formation. Therefore, it is necessary to separate them out from the reaction solution. This can be achieved by washing with water. The repeated washing with water separates the halide content gradually. To preserve the ionic liquid from washing away, 1-bromohexane is added which reduces the water solubility of ionic liquid. The halide content reduction is confirmed with Silver nitrate test.

2.2. Fabrication of sensor

Single walled carbon nanotubes (SWCNTs) with a diameter of 1–2 nm and length of 5 ~ 30 μm were purchased from Chengdu organic chemical Co., Ltd., China (synthesized by Chemical vapor deposition process). Next we prepared a suspension of [C6-mim] PF6-SWCNTs using following procedure—0.5 mg PIL was dissolved in 10 μL DMF followed by the addition of 0.5 mg SWCNTs. The mixture was grounded for 30 min to obtain a black sticky gel. A stable SWCNTs dispersion was finally obtained after sonicating the gel in 150 mL DMF for 5 h. The sensors were fabricated by drop casting of wrapped SWCNTs; about 8 μL of SWCNTs dispersion was pipetted onto the interdigitated gold(Au) electrode patterned $Si0_2$/Si substrates. Sensing film was made from multiple droplet depositions followed by heating the sensors at 60 °C for 1hr to further remove the residual solvent.

The surface morphology of dispersed SWCNTs in DMF solution (a) before and (b) after [C6-mim]PF6-wrap were examined by FESEM (FEI, Nova Nano SEM 450). Structural quality and degree of defects of SWCNTs were analyzed by Raman spectrometer (LabRAM HR 800, Horiba JY) fitted with a peltier cooled CCD detector, and an Olympus BX-41 microscope. The excitation of the samples was performed at 632.8 nm laser light. Measurements were carried out in the back scattering geometry using a 50× LWD microscope objective. The beam was focused at a spot size of 1.19 μm and the power density ($\mu W\,cm^{-2}$) was kept low to avoid any excessive heating on the probe region. UV–vis absorption spectra were recorded with a VARIAN UV–vis spectrometer operating between 400 and 800 nm. FTIR spectra were taken by Bruker system (VERTEX 70V).

2.3. Procedure for determination of sensing response

The electrical measurements were done using electrical characterization unit (Keithley 4200 SCS). Concentration and flow rate of nitrogen dioxide gas were set and maintained by using gas mixing system (Environics 4000, USA). Dry air was used as the carrier gas. Gasses supplied by Sigma Gas Co., and they were of high purity grade (>99.995%). Sample was placed in an airtight sample holder having provision of probe for electric measurement. Initially dry air was flushed in the inlet of the sample holder at 100 sccm flow rate in order to maintain a constant pressure and to remove the residual moisture to dry the sample. The air flow was maintained till the electrical resistance fluctuations stabilized. Once the electrical resistance stabilized, 1 ppm concentration with 100 sccm flow rate of NO_2 gas (mixed with dry air) was then supplied to the sample holder and change in electrical resistance was measured with respect to time. For molecular desorption from SWNTs, sensor were irradiated under UV light source (4.85 eV) to achieve fast recovery.

3. Results and discussion

SWCNT have employed a huge deal of consideration due to their surface properties in terms of large-active surface area, high-stability, and high porosity which directly dependent on the performance of sensor. Quasi one-dimensional structure, surface electron, mostly carbon vacancies, makes it high sensitive nature in the field of sensor applications. In the fabrication route, the dispersion of nanotubes is very important for deposition of nanotube between interdigited electrodes. In order to choose the Ionic liquid as despersion agent for homogenous and stable solution, a sensor was fabricated by drop cast technique and sensing performance was examined. This dispersion was used for the further work.

3.1. Surface morphology study

To understand the quality of SWCNT-IL in DMF solution, FESEM micrographs of pristine SWCNTs and [C6-mim]PF6-wrapped SWCNTs are presented in Fig. 1. The effects of [C6-mim]PF6 on the SWNT disperse in the DMF solution are shown in Fig. 1(b), where as Fig. 1(a) indicates the pristine SWCNT in DMF solution. The improved dispersion efficiency may be explained because of the presence of 1Hexyl-3-methylimidazolium hexafluorophosphate ([C6-mim]PF6), which are supposed to be directly attached to the wall of the SWCNTs and increase the dispersion of the SWCNTs in the solvent. It can be clearly observed in both images that the some [C6-mim] PF6 present on the nanotube surface, which suggests coating of the [C6-mim]PF6 on the SWNT surface due to the covalent interaction.