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Network density tailored standalone-flexible fluorocarbon elastomer/nanocarbon black chemiresistors for 2-propanone field detection

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ABSTRACT

2-propanone is a commonly-used chemical and is a biomarker of diabetic ketoacidosis. Herein, the development of a novel stand-alone chemiresistive sensor with high sensitivity and selectivity for 2-propanone is reported. Fluorocarbon elastomer (FCE)/nanocarbon black (NCB) conducting composites based chemiresistors with different crosslinking densities were synthesized via melt compounding followed by radiation crosslinking. Conducting composites in different parts of the percolation profile were chosen to establish the dependence of 2-propanone sensing response on the conducting network and the radiation cross-linked network. The chemiresistor showed a highly selective response for 2-propanone whereas a considerably lower response was noted for benzene, toluene, xylene, ethanol, methanol and water. The sensing response had a strong correlation with the FCE-analyte interaction parameter (χ_{12}).

1. Introduction

Exhaled breath analysis is envisaged as a promising non-invasive method for the diagnosis of diabetic ketoacidosis [1–4]. Detection of 2-propanone may, therefore, be helpful for the rapid and early diagnosis of diabetic ketoacidosis — a life-threatening emergency during which 2-propanone level builds up to several hundreds of ppm [5,6]. Additional motivation for 2-propanone detection is its wide-range use in different industrial and laboratory settings. Permissible exposure limit (PEL) as per Occupational Safety and Health Administration (OSHA) is 1000 ppm at a time-weighted average concentration for eight hours shift [7]. Acute inhalation of 2-propanone produce narcosis, inflammation of respiratory tract, stomach and small intestine [8]. Unfortunately, 2-propanone is metabolized slowly and may accumulate in the body; therefore, its occupational exposure poses a risk of irreversible health damage [8,9]. Availability of small, reversible, room temperature and low-cost field detector expected to be highly useful in ascertaining that the exposure to the workers is within permissible limits.

Volatile organic compounds (VOCs) such as 2-propanone are generally analyzed using gas chromatography, FT-IR spectroscopy and HPLC, but such techniques are relatively complex, have portability issues, are time-consuming and include high cost [10,11]. Many different approaches can be used to synthesize portable sensors for VOC field detection, namely surface plasmon resonance, chemiresistivity, surface acoustic wave and quartz crystal microbalance [12–18]. Cost, response time, ease of production, real-time monitoring and the possibility of an easy integration into a chemiresistive array are main advantages of chemiresistive sensors over others [19,20]. The development of a low-cost, selective and wide range sensor for 2-propanone has been an active area of recent research. Güntner et al. have developed Si-doped WO_3 nanoparticles based breath 2-propanone sensor that can be used to follow body fat burn rates in real time [21]. Liu et al. reported the development of zirconia/$CdMoO_4$ based gas chemiresistor for 2-propanone detection, having high sensitivity up to 300 ppm at 625 °C [22]. The same group previously reported the development of zirconia/$CdMoO_4$ electrodes for 2-propanone detection with acceptable selectivity at 650 °C [23]. Shao et al. on the other hand,

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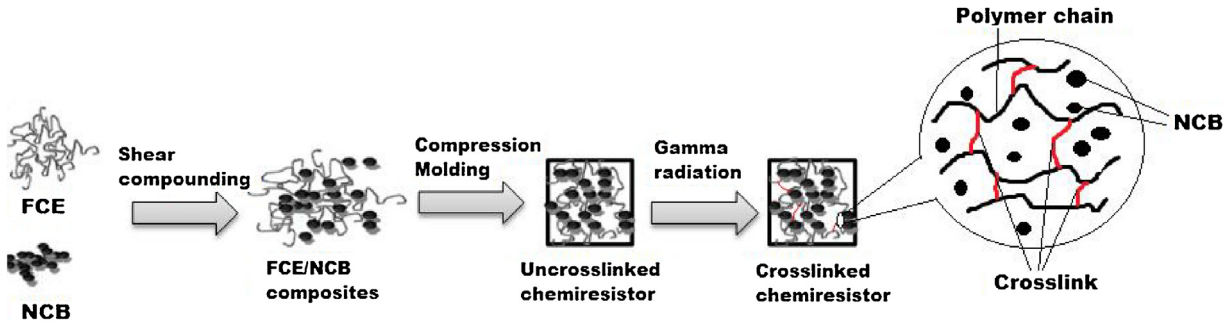

Fig. 1. Schematic of FCE/NCB chemiresistor synthesis protocol (Red lines depict crosslinking). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

exploited the p- to n-type transition in the nanoporous SnO_2 thin film as a function of 2-propanone concentration, to design a 2-propanone sensor [24]. Graphite/polymer composites were also reported to offer a relative change in resistivity of 1.83 to saturated 2-propanone vapour, though not much information was available on low-level detection, sensitivity, and selectivity of such a sensor [25]. All these studies reflect the advances and challenges associated with the development of an effective 2-propanone sensor with wide detection range, low cost, room temperature operations, portability, easy fabrication, and sensitivity. Noteworthily, though some work has been carried out on low-range chemiresistors for 2-propanone, not much success has been achieved in terms of achieving detection range relevant to OSHA's PEL for occupational workers and to the level associated with diabetic ketoacidosis.

Electrical conductivity and a responsive polymer phase are two essential requirements for the development of chemiresistive sensors. Nanocarbon based conducting materials is one of the most promising materials to develop low cost, flexible and standalone chemiresistive sensors [26–28]. Different thermoplastic and elastomeric polymer matrices have been explored for this kind of application. Kumar et al. have reported several conducting polymer nanocomposites (CPC) and studied chemiresistive properties against different analytes [29,30]. They demonstrated that poly(caprolactone)/carbon nanotube (CNT) and acrylate copolymer latexes/CNT are highly useful for sensing of polar VOCs [31]. In another work, Han et al. have used PMMA/SWNT electrospun composites nanofibers combined with inter-digitated electrodes printed on the surface for sensing of methanol vapour [32]. All these studies along with several others highlight the potential of conducting nanocarbon for the development of novel chemiresistive sensors [19,33]. Conducting nanocarbon black (NCB) is an excellent choice as a conducting phase, owing to its low cost and high conductivity [34–36]. Melt and shear compounding are most effective approaches to synthesize CPC as they do not involve any solvent or added chemicals and can be easily upscaled; though there is little information available on its use for chemiresistor development. High energy radiation is an additive-free modality to induce cross-linked networks in a polymer matrix, thus can be a potential tool to tailor analyte diffusion kinetics without significantly affecting polymer-filler interactions. Additionally, such cross-linked networks are expected to improve dimensional stability under chemiresistive pressure, providing an important contribution to the development of a standalone chemiresisitor. In comparison to the substrate based sensors, the standalone sensors are expected to offer advantages such as independence of substrate-sensor interface characteristics, availability of larger surface area and fabrication ease [37].

The present study describes the development of fluorocarbon elastomer (FCE)/NCB based novel chemiresistors, which have high sensitivity and selectivity for the 2-propanone field. High energy radiation was used to achieve different crosslinking densities and the effect of crosslinking density and NCB loading on sensing characteristics was evaluated.

2. Material and methods

2.1. Materials

Fluorocarbon elastomer used was Viton® [66% fluorine; a copolymer of vinylidene fluoride (VF_2) and hexafluoropropylene (HFP)]. Nanocarbon black (NCB) (size 50 nm, surface area 70 m^2/g, density 1.8 g/cc) was procured from M/s TA Corporation, Mumbai, India. 2-propanone, benzene, xylene, toluene and ethylbenzene used were of AR grade (purity > 99.9%) and were procured from local supplier M/s SD Fine Chemicals, Mumbai.

2.2. Sample preparation

FCE/NCB nanocomposites were prepared by shear compounding method. Different amount of NCB and FCE were taken considering their bulk density and was mixed homogenously in Brabender plasticordar at 100 °C, 30 rpm for 20 min. The homogeneous mixture was taken out and cut into small pieces. Then these small pieces were compressed moulded at 150 kg/cm^2 for 30 min at 120 °C into different thicknesses (100 μm–500 μm) with an area of 10 cm × 10 cm. Chemiresistors were cross-linked by exposing them to Co-60 gamma radiation in a gamma chamber (GC-5000) for desired absorbed dose (Fig. 1). Prior to irradiation the dose rate was ascertained by Fricke dosimetry and was found to be 1.0 kGy/h. The samples in the study were mentioned as VTX^Y where X is the wt% of the NCB in the composite and Y is the absorbed dose. NCB content was varied from 10 wt% to 40 wt%. The network density of the nanocomposites was varied by exposing samples to different gamma radiation doses (50 kGy, 100 kGy and 300 kGy). The estimation of network density is described elsewhere [38].

2.3. 2-Propanone mass uptake

For sorption studies, radiation cross-linked composites were Soxhlet extracted for 12 h to extract any sol content using 2-propanone as a solvent. The insoluble gel part was then dried initially under room conditions and later under vacuum at 40 °C. The dried composites so obtained were cut into uniform circular pieces of 1 cm diameter using a sharp-edged die and used for swelling studies. Pre-weighed samples were placed in a 200-mesh stainless steel compartment and immersed in an excess of solvent at the desired temperature. The swollen samples were periodically removed, blotted free of surface solvent using laboratory tissue paper, weighed on an analytical balance (accuracy 0.00001 g) from M/s AND, India, in stopper bottles and returned to the swelling