Sensors and Actuators B 208 (2015) 444–449

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Oxygen plasma treated carbon nanotubes for the wireless monitoring of nitrogen dioxide levels

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ARTICLE INFO

Article history:
Received 18 September 2014
Received in revised form 25 October 2014
Accepted 11 November 2014
Available online 20 November 2014

Keywords:
Carbon nanotubes
Plasma treatment
RFID
Nitrogen dioxide

ABSTRACT

There is a growing interest in the development of smart global systems of wireless, distributed sensors that can be deployed and then operated with no human intervention. However, there are still important technological barriers related to sensor performance and power consumption that limit the implementation of such systems. This paper shows that nanotechnology could help overcome these barriers. An oxygen plasma treatment has been used to functionalise, in a controlled way, the outer walls of multiwalled carbon nanotubes. This treatment respects the integrity of carbon nanotubes but gives rise to carbonyl groups grafted at their sidewalls, which greatly enhance the room-temperature sensitivity and selectivity of the nanomaterial to nitrogen dioxide. The detection mechanism of nitrogen dioxide in the presence of ambient moisture is discussed in light of computational modelling, compositional characterisation and gas sensing tests. The optimised nanomaterial has been used to develop a semi-passive radio frequency identification tag with the capability of sensing nitrogen dioxide in the environment. The tag, which is read by a low-cost commercially available ultra-wideband radar, is normally in sleep mode and includes a wake-up circuit, so power consumption is minimised. This wireless sensor is able to reproducibly detect nitrogen dioxide concentrations from 10 ppm to 100 ppm, with a mean relative error of 0.29%.

1. Introduction

In recent years, hand-held devices for gas detection are getting more and more popular. This entails increasing research activities to develop gas sensors featuring small size, low power consumption and low costs. There is a need for developing grids of wireless, intelligent, autonomous and very low power multisensory systems requiring no human intervention after their implementation, since this would allow setting smart global systems of networked sensors for many different applications. These would include, but are not limited to, monitoring perishable goods along the logistics chain and indoor or outdoor air pollution monitoring [1–3]. Radiofrequency identification (RFID) is a widely extended technology where it is needed to remotely identify an object [4]. It is based on a reader that interrogates one or more tags. The reader acquires their identification (ID) remotely via a radiofrequency (RF) link. Since RFID systems first appeared, a lot of research has been done to improve their capabilities: the aim is to obtain not only the ID, but also parameters of the tag's surrounding physicochemical environment. These parameters are sensed by the tag itself, which becomes a wireless sensor [5]. However, there are still important technological barriers that limit the implementation of smart and autonomous systems with sensing capabilities. These obstacles are related to (i) sensor performance, (ii) power consumption and (iii) size of the system as a whole.

Considering applications related to the environmental monitoring, the detection of nitrogen oxide species, the so-called NO_x (NO or NO_2), is particularly important. Released from combustion facilities and automobiles, nitrogen oxides are known to cause diseases of the respiratory system, catalyse the formation of ozone in the troposphere and be harmful to the environment as a source of acid rain and fog [6,7]. Although some metal oxides have been found to be particularly sensitive to nitrogen oxides [8,9], they need too high an operating temperature, which, combined with their broad

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http://dx.doi.org/10.1016/j.snb.2014.11.059
0925-4005/

cross-sensitivity, has prevented their adoption as sensitive material in wireless sensor systems. Electrochemical NO_x sensors, which are relatively low power and affordable, could represent a good alternative to resistive metal oxides [10]. However, their internal architecture makes them very hard to miniaturise and thus, are not suitable for being used in RFID tags. On the other hand, different studies have shown the excellent potential of carbon nanotubes (CNTs) as sensitive material for detecting biological and chemical molecules [11–14]. Via functionalisation of CNT sidewalls, a selected (or tuned) chemical interaction between specific chemical species and the nanotube surface can be reached and the selectivity of the adsorption process can be enhanced [15–20]. Some properties of CNTs make them very attractive to produce nanosensors for industrial, logistics and environmental applications since (i) their intrinsic strength makes them suited for miniaturised sensors and usable on flexible substrates [21] and, (ii) they respond even when operated at room temperature [22–26], which is optimal for ultra-low power nanosensors to be integrated in battery-operated tags of a wireless system.

Indeed, several groups have reported the detection of gaseous species with CNT-based sensors integrating RFID tags. Tentzeris and co-workers have shown the detection of NH_3 (4 ppm) and NO_2 (10 ppm), however, in this case the tag was wired to the reader and wireless operation was not shown [27]. A passive wireless sensor was presented by Grimes and co-workers for detecting CO_2, O_2 and NH_3 [28]. This system enables measuring at too short a reader to tag distance (15 cm). A sensor for detecting dichloromethane, acetone and chloroform vapours, connected to a Bluetooth module was presented by Reddy and co-workers [29]. However, the Bluetooth module implies high consumption and does not meet the stringent low-power needs of a practical wireless, battery-operated tag with gas sensing capabilities. The detection of ammonia at a reader-to-tag distance of 63.5 cm was reported by Tentzeris and co-workers [30], however, the ammonia concentration tested was very high (100,000 ppm). Finally, the detection of CO_2 employing a chipless RFID sensor was shown by Yamashita and co-workers [31] but, once more, a short reader-to-tag distance (i.e., 20 cm) is needed. All the systems mentioned above use narrow-band signals, which are prone to suffer interferences from other systems such as WiFi, Bluetooth or cellular phones and work only at low reader-to-tag distances.

Here we report the fabrication of a semi-passive RFID sensor system based on oxygen plasma treated multiwalled carbon nanotubes for detecting nitrogen dioxide. Detection and baseline recovery of the sensor is performed at room temperature. The results of the CNT functionalisation procedure are presented and discussed in light of HR-TEM and XPS studies. The sensitivity, selectivity and detection mechanism of treated CNTs is discussed employing experimental findings and density-functional theory (DFT) calculations. The sensor tag is normally in a sleep (low power) mode and includes a wake-up circuit to increase battery life time. The tag also has a self-calibration circuit that enables background subtraction and calibration. This is essential to make measurements in time-varying scenarios. The functionality of the sensors in wireless mode is demonstrated employing as reader a commercially available ultra-wideband radar.

2. Experimental

The multiwalled carbon nanotubes used in the experiment were obtained from Nanocyl, S.A (Belgium). They were synthesised by catalytic chemical vapour deposition and their purity was higher than 95% (Nanocyl^{TM} NC3100). The nanotubes were up to 50 microns in length and their outer and inner diameters ranged from 3 to 15 nm and 3 to 7 nm, respectively. A uniform functionalisation

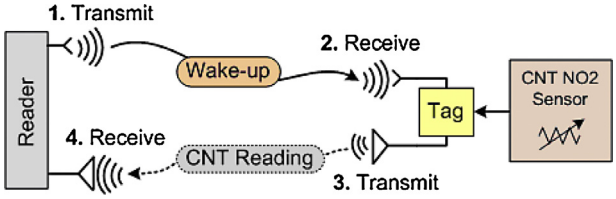

Fig. 1. Scheme showing the wireless nitrogen dioxide sensor set-up.

with oxygen was applied to the as provided carbon nanotubes in order to improve their dispersion and surface reactivity. A home-made magnetron sputtering chamber was used. CNTs were placed inside a glass vessel and a magnet, externally controlled from the plasma chamber, was used to stir the nanotubes. Inductively coupled plasma at a RF frequency of 13.56 MHz was used during the process. Once the CNT powder was placed inside the plasma glow discharge, the treatment was performed at a pressure of 0.1 Torr, using a power of 15 W, while the processing time was adjusted to 0.5, 2 or 5 min. A controlled flow of oxygen was introduced inside the chamber, which gave rise to functional oxygen species attached to the carbon nanotubes sidewalls (i.e., oxygenated vacancies consisting of hydroxyl, carbonyl and carboxyl groups) [32,33]. In the second processing step, the functionalised carbon nanotubes were dispersed in dimethylformamide, ultrasonically stirred during 20 min at room temperature (200 W Ultrasonic Bath, Selecta S.A., Spain) and subsequently air-brushed (JB1113N automatic dispenser and nozzle, Fisnar, Inc., USA) onto interdigited electrodes printed on Rogers RO4003 substrates while the resistance of the resulting film is monitored during the deposition, since this enables us to obtain sensors with reproducible baseline values [34]. During deposition, substrates were kept at 100 °C, which ensured a fast evaporation of the solvent and good adhesion of carbon nanotubes to the substrate. Such temperature ensures the complete evaporation of the solvent in which carbon nanotubes are dispersed when these reach the heated substrate. Lower temperatures would result in the solvent wetting the substrate during the deposition and higher temperatures would result in the solvent being totally evaporated before nanotubes actually reach the substrate. These two situations are undesirable since the former leads to a non-uniform deposition and the latter to poor adhesion of the films. The morphology and composition of plasma treated CNTs was studied by TEM and by XPS, respectively. For TEM analysis, plasma treated CNTs were dispersed in ethanol, and a drop was deposited onto a commercial lacey-carbon grid. The TEM experiments were carried out on a Philips CM20 and an aberration-corrected JEOL JEM-ARM 200F, both operating at 200 kV. The chemical composition of the samples was investigated with X-ray photoelectron spectroscopy (XPS), using the VERSAPROBE PHI 5000 spectrometer from Physical Electronics, equipped with a Monochromatic Al Kα X-Ray. The energy resolution was 0.7 eV. To compensate built-up charge on the sample surface during the measurements, a dual beam charge neutralisation composed of an electron gun (~1 eV) and the Argon Ion gun (≤10 eV) was used.

The proposed wireless sensor uses a battery-powered tag based on Ultra-Wideband (UWB) [35]. The sensor described above is connected to this tag. UWB is known for being robust to interferences from other systems, permits to localise the physical position of the tags within an area, and works at long reader-to-tag distances (up to 8.5 m) [35]. The sensor is normally in a low-power mode until it is woken by the reader. This leads to a current consumption of 20 nA when the sensor is in the sleep mode and 325 μA when it is woken. For a typical situation of 12 measurements per hour and a 1000 mAh battery, the expected lifetime of the sensor tag is about 10 years. Fig. 1 shows a scheme of the wireless system. The reader transmits an interrogation (wake-up) order to the tag. The