Innovative Gas Sensors for Sub-ppm Detection of Organophosphorus Nerve Agents by Chemically Functionalized Nanomaterial Based Electrical Devices

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ABSTRACT

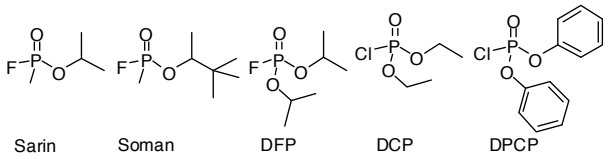
A chemical receptor specific to traces of organophosphorus agents (OPs) has been synthesized and grafted to carbon nanotube or silicon nanoribbon based electrical devices. Our results show that it is possible to detect efficiently traces of OPs with good selectivity notably with the use of silicon nanoribbons by monitoring the Drain-Source current of the SiNR-FET at an optimum back Gate voltage as a function of time.
Keywords: nerve agents • sensors • carbon nanotubes • silicon nanoribbons • nanotechnology

1 INTRODUCTION

The threat of a chemical attack on homeland and military forces continues to grow and recent examples such as Iraqi gas attacks or Tokyo terrorist act have clearly demonstrate that organophosphorous agents are powerful neurotoxic molecules that can actually be used as chemical warfare agents and weapons of chemical terrorism. [1]

Due to the structural diversity of toxic chemicals, there is no single ideal sensor for all potential chemical agents, and many sensors with widely different sensitivities are needed for operational processes. Presently, the methods used to detect organophosphorus nerve agents are mostly inadequate for today's expending requirements. New sensors are highly expected, with improved performances such as low weight, very limited false positive, low power consumption, high sensibility, high selectivity, etc.

The ease of production and extreme toxicity of OP nerve agents underscores the need to detect these odorless and colorless chemicals. Today, there is an important need for wandering applications of selective sensors for organophosphorus (OP) based toxic gases for instance for individual soldier protection. In the same context we have to take into account the urgent need of passive and low consumption multipoint sensors with extremely low rate false alarm for preventing toxic gas attacks that could be installed in public areas such as subway stations, stadiums, malls...



Scheme 1. Chemical structures of some OPs

In this communication we will present new sensing techniques developed for the detection of organophosphorus nerve agents based on the recent developments of nanosciences and nanotechnologies. The miniaturized detectors devices based on electrical detection, i.e. resistors or transistors, using semiconducting parts made either of functionalized carbon nanotubes or silicon nanowires.

2 CARBON NANOTUBE BASED SENSORS

The first kind of sensors we realized where made of single walled carbon nanotubes (SWCNTs) in a resistor configuration. First, the SWCNTs where dispersed in NMP (N-methylpyrrolidone) by ultrasonication for 30 minutes. Centrifugation at 13 000 g afforded a grey solution of SWCNTs suitable for spray coating technique. The substrates are made of gold electrodes, obtained by standard lithography on silicon dioxide. The density of the network

of SWCNTs was controlled by spray duration and controlled by SEM analysis.

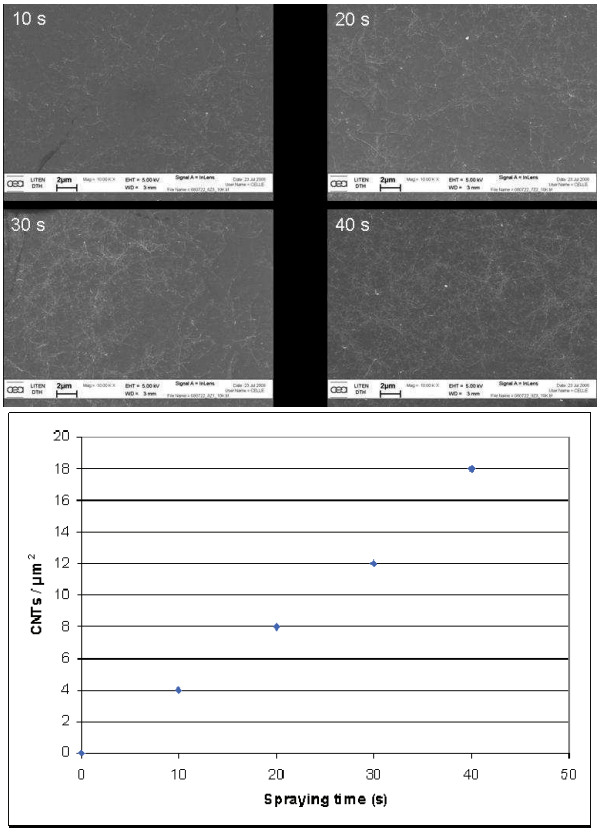


Figure 1. SWCNT network density as a function of spray duration

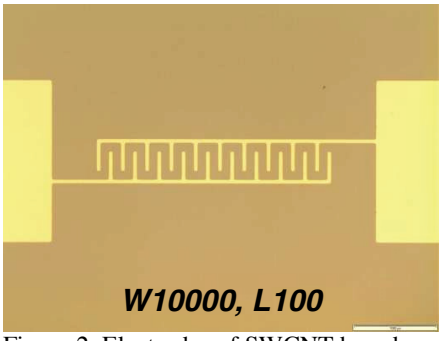
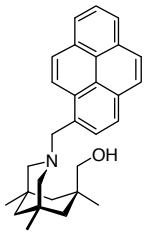


Figure 2. Electrodes of SWCNT based sensors

The as made sensors where then characterized in air and with DiPhenylChloroPhosphate (DPCP, see Scheme 1), a simulant of Sarin-like molecules. The measured vapor pressure of DPCP was around 600-800 ppb in our experimental conditions.

When resistive devices made of pristine nanotubes were exposed to DPCP vapor pressure, an immediate change in resistivity was observed, the intensity increased by about 50 % in 10 minutes. This indicates that SWCNTs are intrinsically sensitive to DPCP, but they are generally sensitive to many analytes. In order to improve the selectivity towards OPs, we modified the carbon nanotubes with the synthesised molecule **1**, originally developed by Rebek et al. [2]



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The pyrene part ensures good stabilizing interactions with SWCNTs whereas the rest of the molecule allows good reactivity towards OPs. Using this functionalization route, the response of the sensor was significantly improved, with a 800 % increase of intensity under identical operating conditions (Figure 3).

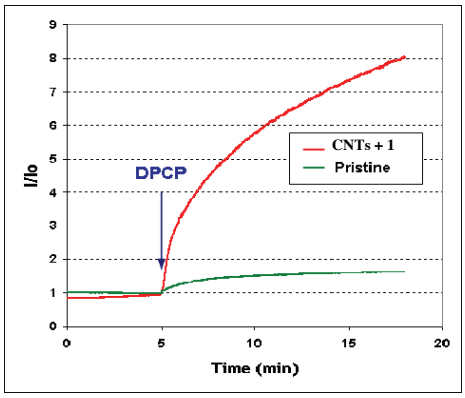

Figure 3. Response of vapor pressure of DPCP by SWCNT based sensors

Other chemical functionalizations gave also satisfactory results and will be presented during the oral communication.

3 SILICON NANOWIRE BASED SENSORS

Silicon nanowires are also interesting semiconducting nanomaterials useful for making very small sensors. We used silicon nanowires fabricated from silicon-on-insulator wafers. Silicon surface can be easily functionalized by different techniques, including thermal hydrosilylation of alkenes or alkynes.

The same reactive moiety was used for functionalization of silicon nanowires, but with an alkyne group as the anchoring species. The synthesis was realized from Kemp's

triacid in only four steps with an overall yield exceeding 50%. The molecule was grafted onto silicon nanowires by thermal hydrosilylation in aromatic solvents, and the as-made molecular monolayer was characterized by contact angle, MIR and XPS. A scheme of the functionalized device is presented in figure 4.

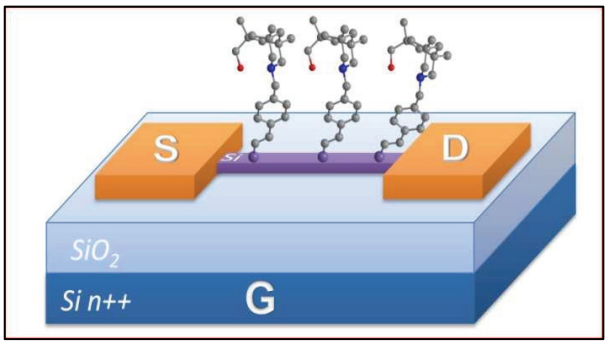

Figure 4. Scheme of the silicon nanowire base sensor (transistor configuration)

The sensitivity of this device in resistive configuration (Vg = 0) was quite good since a significant ten-fold decrease of the resistance R_{SD} was observed upon exposure to vapors of DPCP. When the device was used in transistor configuration, two to four orders of magnitude were measured before and after exposure to OP vapor (Figure 5).

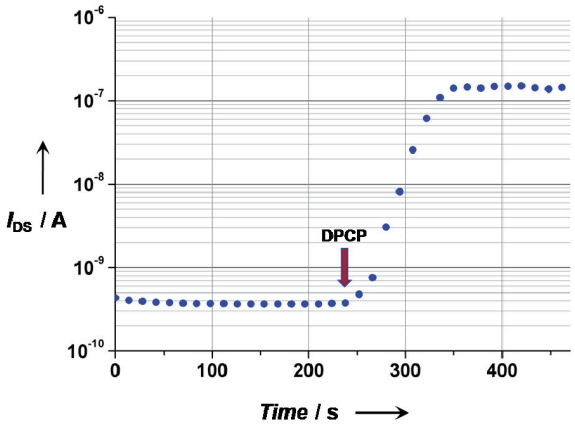

Figure 5. 4x1 μm^2 functionalized SiNR-FET, I_{DS} measured in pulsed mode as a function of time (V_{DS}=–1 V, V_{GS}=V_0=-2 V). DPCP vapors were introduced at t= 240 s.

Furthermore, our first attempts to evaluate selectivity of the SiNR-FETs was rather successful since no significant variation of intensity was observed upon exposure to various organic compounds (cyclohexane, dichloromethane, acetone, acetonitrile, triethylamine, acetic acid…).

In summary, we have developed two kinds of nerve agent sensors based on electrical transduction of a chemical reaction occurring on the surface of a functionalized nanomaterial. Up to now, the best results were obtained with silicon nanowires which showed a very fast and marked response at sub-ppm level of OPs stimulant. We hope this technology of hybrid sensors will help to develop sensitive, compact, low-cost and low-consumption nomade devices for widespread applications in the fields of defense and homeland security.

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