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COMMUNICATION

Chemical functionalization of electrodes for detection of gaseous nerve agents with carbon nanotube field-effect transistors†

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An innovative sensor for the detection of nerve agents in the gas phase based on a carbon nanotube field-effect transistor was developed. A high sensitivity to organophosphorus gases was obtained by modifying gold electrodes with specific tailor-made self-assembled monolayers.

The advent of international terrorism requires us to prevent potential attacks. In particular toxic gases are amongst the simplest materials to use and can lead to tragic consequences.[1] Organophosphorus compounds (OPs) are extremely neurotoxic compounds. They have already been used, like for instance Sarin during the attack of Tokyo's subway in 1995. Several new sensing concepts have recently been reported for the detection of these chemical warfare agents including colorimetric and fluorimetric spectroscopies,[2–4] chemiresistors,[5,6] enzymatic assays,[7] gas chromatography/mass spectrometry,[8] microcantilevers,[9] ion-mobility spectrometry[10] and others. However, there is still a need for highly sensitive and low-cost sensors. Since the pioneering work of Dai[11] and Snow,[12] carbon nanotube field-effect transistor (CNTFET) based sensors have been shown to be good candidates for the detection of gas traces.[13,14] Their effectiveness is mainly ascribed to an extreme sensitivity to electrostatic changes at the surface of the CNTs and/or an alteration of the Schottky barrier at the CNT/metal interface. A recent work described the use of OP sensitive molecules anchored on silicon nanowires in which the reaction of a primary alcohol with an OP initiates an intramolecular cyclization to generate a quaternary ammonium salt. This leads to a detectable charge formation in the vicinity of a semiconductor.[15]

It is now well established that self-assembled monolayers (SAMs) can drastically modify the work function of gold electrodes.[16–18] We thus chose to create OP sensitive electrodes by synthesizing specific molecules, and grafting them onto electrodes of highly sensitive CNTFET transducers.

The sulfur-containing reactive moiety towards OP agents, **3**, was prepared in 2 steps from the scaffold of 1,5,7-trimethyl-3-azabicyclo[3.3.1]nonane-7-methanol (**1**).[15]

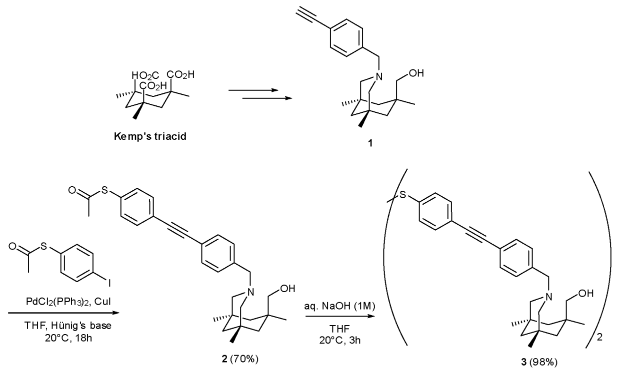
In this communication, we report the fabrication of CNTFET sensors modified at the electrode with organic species very sensitive to OPs, and their characterization with the Sarin simulant, namely diphenylchlorophosphate (DPCP).

In order to graft the reactive species onto gold electrodes, we first prepared the thioacetate precursor **2** by Sonogashira coupling of **1** with 4-iodo-phenylthioacetate (Scheme 1). However, molecule **2** is not stable. Even stored in the solid state and at low temperature, this compound undergoes intermolecular transesterification which generates by-products.

Therefore, we synthesized the corresponding disulfide **3** in high yield from **2** by treatment with sodium hydroxide. The compound **3** is stable for months and allows efficient formation of SAMs on gold. Its structure was unambiguously supported by ^{1}H and ^{13}C NMR, IR spectroscopy and mass spectrometry.

SAMs of tolane disulfide derivative **3** on a gold-coated silicon wafer were obtained by immersing the gold surface overnight in a freshly prepared 0.7 mM solution of acetone at room temperature.

The water contact angle of the sample (86.6 ± 3.7°) is consistent with the literature data.[19] Furthermore, the grafting of molecules on gold was also confirmed by XPS experiment (see ESI†). Exposure to vapours of DPCP induces a significant downshift of the contact angle (72.8 ± 4.4°), in agreement with a higher hydrophilic surface obtained after reaction.



Scheme 1 Synthesis of **3** from Kemp's triacid.

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† Electronic supplementary information (ESI) available: Synthesis of molecule **3**; preparation of monolayer and characterization by contact angle and XPS; device fabrication; carbon nanotube dispersion and spreading; KPFM measurements. See DOI: 10.1039/c1cc11517k

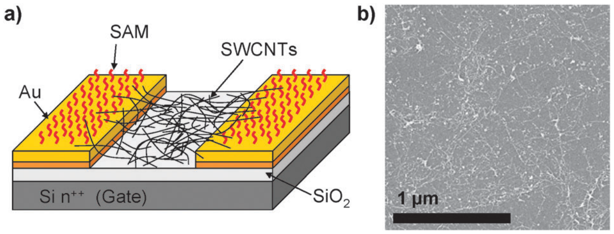

Fig. 1 (a) Schematic structure of the CNTFET with gold electrodes functionalized by **3** (b) SEM image of the SWCNT network.

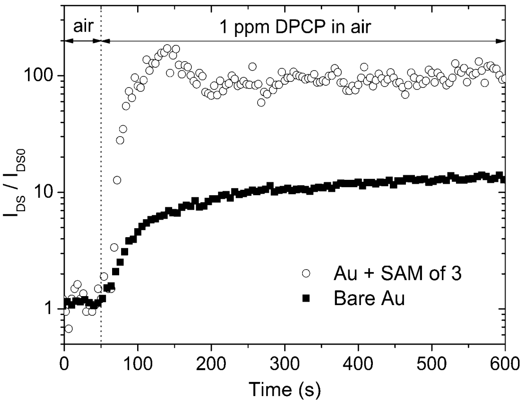

Fig. 2 Normalized response to the CNTFET sensors upon exposure to DPCP vapours with bare Au electrodes (squares; V_{DS} = −1 V, V_{GS} = 10 V) and Au electrodes functionalized with **3** (circles; V_{DS} = −1 V, V_{GS} = 4 V).

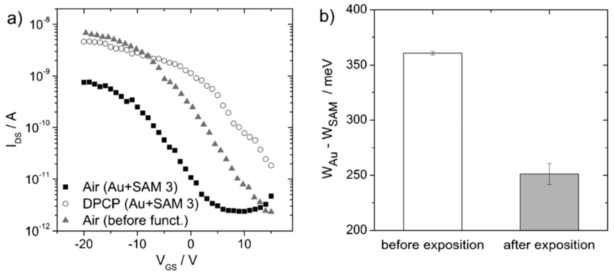

Fig. 3 (a) Transfer curves of CNTFET before (grey triangles) and after (black squares) functionalization of electrodes with **3**, and after exposure to less than 1 ppm of DPCP (white circles). (b) Work function variation of gold electrodes functionalized with **3** before and after exposure to DPCP vapours (KPFM measurements).

Devices with bottom gate/bottom contact geometry (Fig. 1a) were fabricated on a heavily doped (100) silicon wafer (n^{++}, 2–5 mΩ cm) covered by a thermally grown silicon dioxide layer (100 nm). The source and drain electrodes of the device were patterned by optical photolithography, followed by Ti (5 nm) and Au (30 nm) evaporation and lift-off. The length and width of the CNTFET channels are respectively 10 µm and 1000 µm.

A spray-coating technique was then used to spread SWCNT (CoMoCat SG65) networks on the device from a dispersion of SWCNTs in N-methylpyrrolidone prepared by sonication and centrifugation (Fig. 1b). Functionalizaton of the CNTFET gold electrodes was performed as described above. Electric measurements were performed on a home-made probe station with an Agilent 4155C semiconductor parameter analyzer. Devices were exposed to DPCP vapours below 1 ppm concentration in air. Experiments were initially carried out using dry air in order to avoid potential hydrolysis of DPCP, however experiments realized with relative humidity ranging from 0 to 90% showed similar detection behaviour. The sensors with and without sensitive SAM were electrically characterized before and after exposure to DPCP to determine the best value of V_{GS} (gate-source voltage) to apply in direct monitoring of OP traces. The transfer characteristics (I_{DS} *vs.* V_{GS}) were measured by applying $V_{DS} = -1$ V as drain-source voltage while sweeping the gate voltage V_{GS} from +15 to −20 V.

Fig. 2 shows on a logarithmic scale the responses of CNTFET devices as a function of time at optimized V_{GS}, with bare and functionalized gold electrodes.

Pristine CNTFET sensors exhibit sensitivity to DPCP vapours with an increase of the current by a factor ~13 and a time constant τ of 198 s, as determined by fitting the experimental curve with an exponential function derived from mass action model.[20] Interestingly, after gold electrode functionalization with **3**, the response of CNTFET to DPCP vapours was highly improved. Current increases much faster (τ ~10 s) and the I_{on}/I_{off} ratio reaches a factor of ~100.

Fig. 3a shows typical transfer curves of CNTFET before (triangles) and after (squares) functionalization of the electrodes, and after exposure to less than 1 ppm of DPCP in air (circles).

After the gold electrode functionalization, a significant decrease is observed for the "ON" current suggesting an increase in the Schottky barrier for holes,[21] for instance as due to a decrease of the gold electrode work function (WF). The quaternary ammonium species generated after DPCP exposure could alter the dipole layer of the monolayer and thus return the work function of gold electrodes towards its initial value (*i.e.* reduce the Schottky barrier for holes), resulting in an enhancement of the current. To check variations in the gold electrode work functions, we carried out Kelvin probe force microscopy (KPFM) measurements on control samples (see details in ESI†). The KPFM results shown in Fig. 3b confirm this hypothesis. After the functionalization with **3**, the WF is reduced by *ca.* 360 meV (reference is the bare Au electrode). After reaction with DPCP, the WF increases by about 110 meV, leading to a WF difference of *ca.* 250 mV compared to bare Au. Since the WF did not completely return to its initial value (bare Au), these WF variations cannot totally account for the fact that the drain current after reaction with DPCP returns to, or even overcomes, the initial value. It is likely that other mechanism(s) need to be taken into account. For instance, a gas-induced doping of the CNTs caused by an electron charge transfer from CNT to the ammonium–an electron acceptor–could also explain the shift of the transfer curves towards positive voltage observed in devices with bare and functionalized electrodes.[11]

In summary, we report an innovative sensor based on CNTFET using electrodes functionalized with a SAM of OP sensitive molecules. The main sensing mechanism is ascribed to the modification of the Shottky barrier at the gold-SWCNT interface when OP compounds chemically react with the receptors, and thus alter the work function of the gold electrodes.

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