



# In situ synthesized carbon nanotube networks on a microcantilever for sensitive detection of explosive vapors

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## ABSTRACT

This paper reports a chemical sensor that consists of a suspended microcantilever and a carbon nanotube (CNT) network that is in situ synthesized on the microcantilever. The in situ synthesis achieves minimized thermal resistance of the interface between the CNTs and the microcantilever, which together with the low thermal mass and the high thermal conductivity allows the sensor to operate in microcalorimeter mode. By heating the CNT networks with an integrated heater, the explosive vapors adsorbed on the CNT surfaces are ignited to deflagration, which releases extra heat to deflect the microcantilever and thus changes the resistance of an integrated piezoresistor. This thermal-mechanical coupling transduction mechanism bridges the heat changes on the CNT networks and the mechanical deflection of the microcantilever. The large surface to volume ratio of CNTs enables fast adsorption of the chemical sensor to explosive vapors and improved equivalent limit of detection (LOD). An equivalent LOD of 2.4 pg is achieved for TNT detection, and run-to-run repeatability and device-to-device reproducibility are better than 4% and 10%. The preliminary results demonstrate the feasibility of development of sensitive CNT chemical sensors using in situ synthesized CNT networks and thermal-mechanical coupling transduction mechanism.

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## 1. Introduction

Detection of explosives, such as 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), is a rapidly increasing task in forensics, anti-terrorist activities, global de-mining projects, and environment monitoring. Most of these applications, if not all, need portable detection technologies with low LOD, high selectivity, and fast response time. However, it is still a technical challenge to fulfill these requirements due to the extremely low vapor pressures of explosives, complex interferences, and various kinds of explosives.

Among the large variety of detection technologies, miniaturized sensors based on micro and nano technologies have attracted considerable research attentions in recent years. In nano regime, carbon nanotubes (CNTs) has promised unprecedented opportunities for developing trace explosive sensors. Due to the high electronic conductivity for electron transfer reactions, CNTs have been used to modify the electrodes of electrochemical sensors to enhance electrochemical signals [1]. For example, multi-wall CNT (MWCNT) and Cu-single walled CNT (SWCNT) have been employed to modify glassy carbon electrodes (GCE), and electrochemical

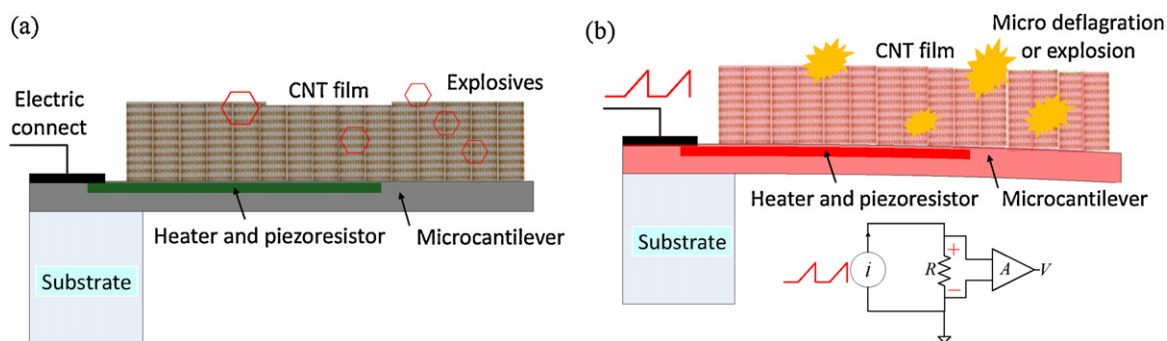
sensors with TNT detection limits down to 0.6 μg/l and 1 ppb have been reported for 10 min preconditioning [2,3].

Individual CNTs and CNT networks have also been exploited to develop a large variety of chemical sensors with different configurations and transduction mechanisms such as FETs [4,5], chemiresistor [6], thin-film-transistor (TFT) [7,8], and optical detection [9]. High-performance chemical sensors using individual CNTs have been realized for detection of TNT in aqueous solution with a LOD of 1 fM [22] and nitrotoluene vapors with a LOD of 262 ppb [10], and they are facing the challenges of variation in electrical properties [11], manufacturing difficulties [12], and poor reproducibility [13,14]. Randomly distributed CNT networks, which are able to mitigate the deviations by averaging the electrical heterogeneity of individual CNTs [15,16], have attracted considerable research attention more recently to develop sensors for various volatile organic compounds (VOCs), nerve agents, and explosives [17–20]. To improve selectivity, metal nanoparticles [21] and self-assembled monolayers (SAMs) [22] of ligands, lipid membranes and peptide receptors, and conjugated polymers have been developed as surface coating reagents to functionalize CNT sidewalls to selectively detect TNT [22,23].

In micro scale, microcantilever sensors with SAMs immobilized on the surfaces have been extensively investigated for explosive detection by measuring either the deflection or the resonance

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**Fig. 1.** Schematic illustration of the sensor configuration and the operation principle. (a) Explosive vapors adsorbed on the CNT sensors. (b) Heating explosive vapors to micro deflagration.

frequency shift induced by adsorption of target chemicals [24]. Microcantilevers operated in bending mode has achieved a LOD of 300 ppt for detection of 2,4-dinitrotoluene (DNT) using a self-assembled layer as receptors [25]. Microcantilevers coated with 4-mercaptobenzoic acid monolayer have been developed for detection of PETN and RDX vapors with LODs in the level of 30 ppt or a few femtograms [26]. To improve selectivity and sensitivity, nanomaterials such as nanoporous framework materials [27] and nanoporous zeolites [28,29] have been employed as surface coaters for detection of explosives or VOCs. A microcantilever with post-transferred MWCNTs have been developed, and by grafting special sensing groups on CNT sidewalls, a LOD of 4.6 ppb has been obtained for TNT detection [30]. Even selective coaters are used, microcantilevers based on chemical receptors normally suffer from interferences such as water molecules that occur at concentrations in the orders of magnitude higher than explosives.

Microcalorimeters, which has been thoroughly investigated for measuring the thermal properties of chemical and biological reactions by analyzing the exothermic and endothermic characteristics of thermal reaction [31–33], were first employed for explosive detection in 1999 [34]. Thanks to the capability in measuring the thermal fingerprints of explosives, microcalorimeters are evolving as an important technique for trace explosive detection. Microcalorimeters with LOD down to 6 pg for TNT detection [35–40] and 3 ppm for combustible gases [41] have been achieved. However, the low volatility of most explosives and the small surfaces of the microcalorimeters need long times to adsorb enough explosives for detection, normally around several tens to hundreds seconds [35].

To overcome the shortcomings of microcantilevers using chemical receptors, this paper reports a microcantilever sensor with integrated CNT networks for explosive detection. The CNT networks are the in situ synthesized on the microcantilever surface rather than self-assembled (post transferred). Direct synthesis enables very low interface thermal resistance between CNTs and microcantilevers, and thus allows the microcantilevers to operate in micro-calorimetry mode by measuring the microcantilever deflection induced by the heat released from the deflagration of the TNT molecules adsorbed on the CNT surfaces. Since micro-calorimetry is able to detect the thermal fingerprints of explosives without the need of chemical receptors, the microcantilevers integrated with CNT networks avoid chemical receptors that are inevitable in normal microcantilever sensors for selectivity, and thus it is possible to achieve short recovery time, reusability, and immunity to interferences and sensor poisoning. Compared with literature reported microcalorimeters, the proposed sensor integrates CNT networks to efficiently adsorb TNT vapors for fast adsorption and detection by exploiting the extremely large surface areas of CNTs.

## 2. Configuration and operation principle

The sensor is a suspended bi-material microcantilever that consists of two silicon dioxide layers and a silicon layer sandwiched in between. Two silicon resistors fabricated in the silicon layer act as a heater and a piezoresistor. A CNT film is in situ synthesized on the surface of the microcantilever. When the chemical sensor is exposed to explosives, the vapors are adsorbed onto the CNT surfaces, as shown in Fig. 1(a). By heating the microcantilever to the deflagration temperature of the explosives using the integrated heater, the CNT film is heated simultaneously to almost the same temperature due to the extremely high thermal conductivity. Thus, the vapors adsorbed on the CNTs are ignited to deflagration, which is an inherently exothermic process and generates a heat increment to the CNT film. This extra heat is conducted to the microcantilever and results in bending of the microcantilever as a result of bi-material structure, which can be detected by the integrated piezoresistors, as shown in Fig. 1(b). Using this thermal-mechanical coupling transduction mechanism, the explosives can be detected by measuring the microcantilever deflection induced by the micro-deflagration.

The transduction mechanism is based on the excellent thermal properties of the microcantilever and the extraordinary physical properties of CNTs. The extremely low thermal mass (around 10 nJ/K [42]) and the low thermal dissipation of the microcantilever allow it to be heated to several hundreds of degrees in milliseconds by the integrated heater to ignite the adsorbed explosive vapors, and allow a distinct deflection to be generated by the infinitesimal heat released from micro-deflagration. The high thermal conductivity of CNTs and the low interface thermal resistance between the microcantilever and the CNT networks, which is critical to achieve high sensitivity that is proportional to the heating rates. The huge surface to volume ratios of CNTs, as well as the fact that the aromatic explosives tend to be physisorbed onto CNTs through  $\pi$ -stacking interaction [43], enhances the adsorption ability to TNT vapors.

## 3. Sensor fabrication

The microcantilever is fabricated from a silicon-on-insulator (SOI) wafer [44]. Integrated heaters and piezoresistors are fabricated on the SOI device layer by ion implantation, which together with a buried oxide layer and a silicon dioxide passivation layer constitutes the mainbody of the microcantilever. The CNTs are locally synthesized on the surface of the microcantilever using a custom-built laser-assisted chemical vapor deposition (LACVD) system [45]. The extremely small heat mass and the minimized thermal dissipation allow the microcantilever to be heated rapidly to high temperatures (600–800 °C) for CNT synthesis by focusing a

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