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Highly sensitive, transparent, and flexible gas sensors based on gold nanoparticle decorated carbon nanotubes

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ABSTRACT

We report on a high performance flexible and transparent chemical sensor based on functionalised single-walled carbon nanotubes (SWCNTs). The SWCNT films were spray-deposited on transparent and flexible plastic substrates, and subsequently decorated with Au nanoparticles (AuNPs) providing a facile and cheap fabrication route. The electrical resistance of the films changed remarkably upon exposure to ammonia (NH_3), AuNP decoration enhanced sensitivity to 255 ppb (parts-per-billion), one of the lowest reported so far. The reported sensor performance is a huge improvement towards low power consumption and its room temperature operation augers well for use in mobile devices for environmental protection and air quality control.

1. Introduction

There exists an increasing worldwide demand for sensors, in particular for standalone and mobile systems, which call for small, low power and flexible devices. Generally nitrous oxide (NO_x) and ammonia (NH_3) are model compounds for gas sensing due to their oxidising and reducing properties. Metal–oxide–semiconductor (MOS) and solid electrolyte (SE) sensors with typical detection limits of 1–1000 ppm at an operating temperature of a few hundred degrees Celsius are commercially available [1–5]. Although these types of sensors are inexpensive and robust, they do suffer from high energy consumption and cannot be fabricated on flexible substrates.

In recent years, nanowires [6–10] and single-walled carbon nanotubes (SWCNTs) [11–13] have been shown to act as ultrasensitive chemical and biological sensors because of their large surface-to-volume ratio with unique physical and electrical properties. Chemical field-effect transistors (ChemFETs) or chemically modified resistors (chemiresistors), in which nanotubes or nanowires act as the conduction channel between two electrodes, work at room temperature and, therefore, have low power consumption. The conductivity of the channel is changed by chemical doping, which can be measured electrically. For SWCNTs, the π-electron system is fully exposed [14] and, therefore, their electrical properties are extremely sensitive to charge transfer and chemical doping from adsorbing species. So far gas and aqueous solution sensors with detection levels of the order of ppm or sub-ppm have been reported [15]. This matches commercial metal oxide film sensors at room-temperature, avoiding the energy intensive operation at elevated temperatures. Furthermore, SWCNT films can be produced cost effectively by spraying into transparent and flexible films, qualifying them for an extended range of applications.

However, SWCNTs are generally grown as mixtures of semiconducting and metallic nanotubes. This can be critical for sensitivity, reproducibility, and reliability. When using large networks of SWCNTs, this problem averages out to a certain extent. However, for thicker films the detection limit rises as the inner tubes are blocked from interacting with target molecules as they cannot penetrate into the network [11]. Thus, it is important to be able to create thin, but well conducting networks and avoid aggregation of the SWCNTs into bundles during deposition [16]. Despite the low sensitivity of network film structure sensors, their simplicity and low production cost make these devices suitable for fabrication processes. Recently, various functionalisation types such as metal particle [17,18] and

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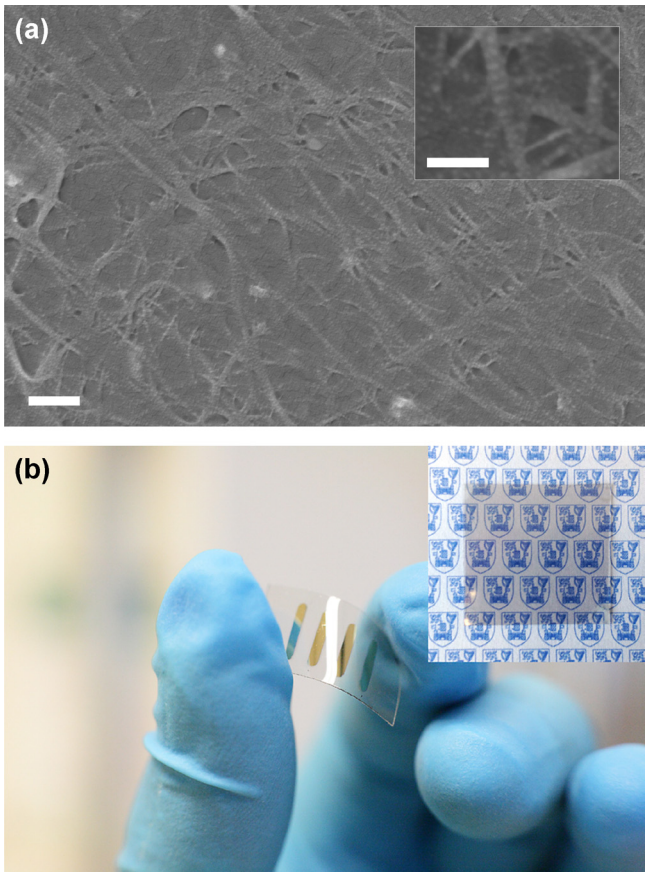

Fig. 1. (a) SEM image of AuNP decorated SWCNT network on the PET substrate. The tiny white dots, indicating Au nanoparticles, typically have a lateral size of ~10 nm, thoroughly covering the surfaces around individual SWCNTs (scale bar = 200 nm). Inset: a higher magnification SEM image with arrows indicating AuNP (scale bar = 100 nm). (b) Optical images of a transparent and flexible SWCNT network film before (inset) and after electrical contacts deposition. The transferred SWCNT film on the PET substrate is highly flexible and clearly transparent apart from the reflective electrodes.

polymer [19–21] have been reported to improve the performance and sensitivity of nanotube based sensors. It is expected that metal clusters display a full range of reactivity with different molecules and show promise for further functionalisation for high analyte selectivity by attaching specific receptors [22]. Furthermore, transparent and flexible substrates are applicable to SWCNT films for plastic electronics [23].

Here, we present transparent and flexible SWCNT film sensors for the detection of NH_3. In the chemiresistor structure, AuNP decorated SWCNT network films are highly sensitive to chemical doping effects. Through the use of polyethylene terephthalate (PET) film support instead of conventional substrates, our sensors are highly flexible and nearly transparent as only the metal electrodes are reflective.

2. Materials and methods

Commercial SWCNTs (Iljin Nanotech) were used to make network films. The as-received SWCNTs were dispersed in water using surfactant-assisted ultrasonication, followed by centrifugation to remove agglomerates and, finally, spray-coated onto PET substrates as described in previous work [16]. The as-prepared SWCNT films were decorated by electron-beam evaporation (CHA Mark 50) targeted at 1 nm Au at a pressure of $\sim 3 \times 10^{-6}$ Torr. As a result, AuNPs with typically lateral size lower than 10 nm uniformly covered the surfaces around each individual SWCNT (Fig. 1(a)).

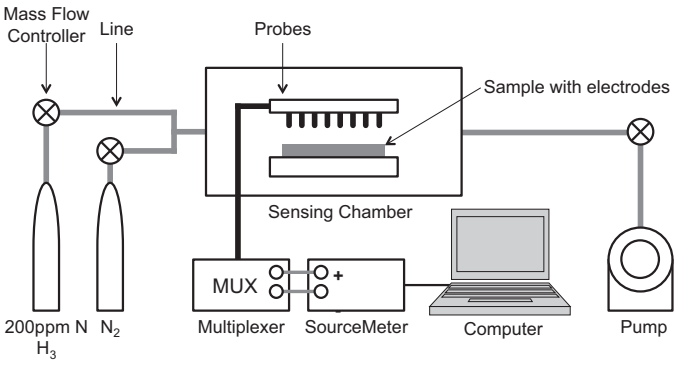

Fig. 2. Schematic of experimental setup for gas sensing.

Electrical contact electrodes of 40 nm Au atop an adhesion layer of 20 nm Ni were deposited by sputtering to create intimate electrical contact. For gas sensing tests, the SWCNT film was placed on a custom-made chip-carrier and Au wires were connected between electrodes of the sensor and bonding pads of the chip-carrier using silver epoxy (DuPont 5007E). As arrayed samples enabled multiple parallel test for improvements of the selectivity and the statistical confidence [24], a multiplexer was attached to our gas sensing system for simultaneous parallel measurement (Fig. 2).

In this study, the AuNP decorated SWCNT films were loaded in a sensing chamber at a pressure of 9.4 Torr and NH_3 gas was introduced with dry N_2 as carrier gas at a constant flow rate of 100 sccm (standard cubic centimetres per minute). The electrical resistance was measured at a constant bias voltage of 0.1 V and all sensing tests were carried out at room temperature. In every measurement, the sensor was exposed to dry N_2 for 1 min to record initial resistance and then NH_3 balanced with N_2 was introduced for 2 min to observe the sensor response. The sensor was exposed to dry N_2 for 5 min to recover and this gas sensing sequence was periodically repeated four times. Imaging was performed with a Zeiss Ultra HRSEM (high resolution scanning electron microscopy) at an accelerating voltage of 3 keV. A thin film of Pt was sputtered onto the samples to avoid charging effects during SEM imaging.

3. Results and discussion

Our SWCNT films on PET substrates are transparent and flexible as shown in Fig. 1(b). The photograph shows a bent film on a PET substrate with four Au electrodes clearly visible. The inset shows a film without electrodes on a coloured background underlining its transparency.

The SEM image (Fig. 1(a)) shows a homogenous network of SWCNTs with some small bundles visible. The fine dispersion is due to our optimised spraying process and important for high conductivity and, also, for a high surface exposed for AuNP decoration. The inset shows the film after AuNP decoration. The small white dots are AuNPs with a typical radius of ~5 nm, attached to the circumference of individual SWCNTs or bundles.

The source-drain current versus source-drain voltage ($I_{ds} - V_{ds}$) characteristics of a bare SWCNT film and a AuNP decorated SWCNT film are shown in Fig. 3(a). Small differences in the resistance of the SWCNT film in 2-/4-probe configurations indicate that the electrodes are well-defined with low contact resistances between the SWCNT network and metal electrodes as very linear $I_{ds} - V_{ds}$ curves are observed. It is well-known that SWCNTs behave like p-type semiconducting materials in atmosphere, giving good contact to Ni. The resistance of all films is roughly 1.7 kΩ with an infrared transparency of >95% [16]. It is important to note that the high process reliability of our SWCNT films is crucial for