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# Hybrid gas sensor based on platinum nanoparticles/poly(methyl methacrylate)-coated single-walled carbon nanotubes for dichloromethane detection with a high response magnitude

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ABSTRACT

A dichloromethane (DCM) sensor with a high response magnitude was successfully fabricated using the integration of single-walled carbon nanotubes (SWNTs), poly(methyl methacrylate) (PMMA) and platinum nanoparticles (Pt NPs). A pristine SWNT network was first formed by drop-casting onto printed circuit board (PCB) substrates. Next, PMMA was coated onto the pre-dropped SWNT network by spin coating using a PMMA-toluene solution, followed by the deposition of Pt NPs by electron-beam evaporation (hereafter referred to as Pt/PMMA/SWNT). The Pt/PMMA/SWNT enabled an approximately 69-fold improvement in DCM detection compared to pristine SWNT. The high response magnitude of the Pt/PMMA/SWNT was successfully achieved because of the incorporation of PMMA and Pt functions. Swelling of the PMMA matrix as a result of DCM adsorption leads to PMMA volume expansion, thereby increasing the SWNT-SWNT distance, which results in an increase in the resistance. Pt NPs promote the dissociation of DCM to CO, and consequently the CO oxidation on the Pt NPs catalyst and electron donation from Pt NPs to SWNTs, resulting in an increase in the resistance. Moreover, a linear relationship was obtained between the sensor response of the Pt/PMMA/SWNT and the concentration of DCM. These results suggest that the integration of SWNTs with PMMA and Pt NPs is a promising approach for improving DCM detection at room temperature.


## 1. Introduction

Volatile organic compounds (VOCs) [1] have been widely used in various industrial processes and commercial products, such as transport, household chemicals, paints and adhesives. Several VOCs are directly harmful to environmental and human health even at trace levels in ambient air. For example, dichloromethane (DCM, $CH_2Cl_2$), which is mainly used in the metal surface degreasing and electronics industry, is known as the cause of respiratory and central nervous system, chronic toxicity and carcinogenicity [2–4]. Hence, environmental monitoring and industrial safety are absolutely crucial for the protection of environmental and human health. Since the last decade, the most widely used analytical methods for VOC detection have been gas chromatography/mass spectrometry (GC/MS), high-performance liquid chromatography (HPLC) and photoionization detection (PID) because of their high sensitivity and reliability. Nevertheless, their practical application is highly limited as a result of their complexity, relatively high cost, unportability and calibration requirements to maintain accuracy. Recently, a gas sensor based on the simple change in its resistance in response to analytes has become a promising candidate for practical sensing devices. The advantages of a gas sensor include its compact size, real-time monitoring and low power consumption. Gas sensors based on metal oxide materials have been widely developed for VOC detection with a detection limit down to the parts per million (ppm) level [5,6]. Despite their high sensitivity, these sensors exhibit drawbacks, including nonselectivity and high power consumption (operating temperature > 200 °C). Several nanostructured materials, such as single-walled carbon nanotubes (SWNTs) [7], have attracted considerable attention as alternative sensing materials because of their distinctive characteristics in structural, electrical, optical, mechanical and thermal properties. SWNTs have shown outstanding potential for gas sensing

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applications because of their well-organized nanostructure, large specific surface area [8] and electrical properties [9,10]. SWNT-based sensors have demonstrated high response to oxidizing gases down to the parts per billion (ppb) level under room-temperature operation [11–14]; however, they are weakly sensitive to VOCs. In recent years, to overcome these obstacles, many efforts have been made aiming to improve the VOC sensing performance of such sensors by means of SWNTs functionalized with polymers [15–18] and metal nanoparticles (NPs) [19–21]. For instance, a gas sensor based on functionalized-multi-walled carbon nanotubes and poly(methyl methacrylate) composites (f-MWNT-PMMA) by dip-coating technique has been demonstrated for VOC detection [15,16]. This f-MWNT-PMMA-based sensor shows a high response to a saturated vapor of DCM [15] but a low sensor response to DCM vapor in a partial pressure range of 27–273 Torr [16]. In addition, MWNTs were functionalized using potassium permanganate with the help of a phase transfer catalyst. Although the major advantage of this process is a high yield of functionalized MWNTs, but it is time-consuming and involves the use of hazardous chemicals. Another type of gas sensor was fabricated using conductive polymer-MWNT composites by spray layer by layer (sLbL) without further treatment of MWNTs for VOC detection at a saturated vapor [17]. Recently, W. Muangrat et al. [18] demonstrated a simple preparation of gas sensor by spin-coating PMMA on the drop-casted SWNTs (PMMA/SWNT). The sensor response of PMMA/SWNT to DCM greatly increases 5.4-fold higher than that of pristine SWNTs. The sensing mechanism of the polymer-functionalized carbon nanotubes (CNTs) is attributed to the swelling of the polymer matrix upon exposure to the organic vapor molecules, leading to volume expansion, and thereby giving rise to an increase in the CNT–CNT distance, resulting in an increase in the resistance. Additionally, the deposition of palladium (Pd) and platinum (Pt) nanoparticles (NPs) on MWNTs enhances the sensor response toward aromatic VOCs (benzene and toluene) and non-aromatic VOCs (acetone, ethanol and methanol) [21]. The sensing mechanism of metal NP-decorated CNTs can be explained by the electron transport from the metal NPs to the CNTs, resulting in an increase in the resistance. As mentioned above, polymer and metal NPs are effective in improving VOC sensitivity by different mechanisms. Thus, utilizing the functions of both the polymer and the metal NPs in a single device is a promising route to improving its VOC sensitivity and response magnitude.

In this work, we successfully demonstrated highly sensitive detection of DCM vapor under room temperature conditions by means of SWNTs functionalized with PMMA and Pt NPs without further SWNT treatment. The response magnitude of the hybrid sensor to DCM was 69-fold higher than that of pristine SWNTs and linearly increased with increasing DCM concentration. The sensing mechanism was elucidated by catalytic oxidation on the Pt NPs catalyst surface and polymer swelling. The proposed hybrid sensor shows figures of merit over the previous reports in terms of the simplicity in sensor fabrication and the enhancement of the sensor response magnitude to VOCs at the concentration lower than a saturated vapor.

## 2. Experimental methods

### 2.1. Fabrication of gas sensor device

A printed circuit board (PCB) consisting of an interdigitated Cu/Au electrode with a gap of 250 μm was used as the sensor platform. An SWNT suspension was prepared by dispersing SWNTs, (diameter and length in the ranges of 1.2–1.5 nm and 2–5 μm, respectively) in 1,2-dichloroethane by ultrasonication for 3 h and subsequently dropping onto the PCB. The electrical resistance of the SWNT on the PCB was adjusted to approximately 100 kΩ. A solution of PMMA ($M_w = 94{,}600$ g/mol) was prepared in toluene and stirred for 24 h. Then, the PMMA solution was spin-coated onto the predropped SWNT network at a spinning speed of 3000 rounds per minute for 5 min, followed by heating at 100 °C for 24 h to eliminate the solvent in the sensor samples. The PMMA concentration was varied between 1 and 5 wt.%. Next, the prepared PMMA-coated SWNTs were deposited with Pt NPs by electron-beam evaporation. The amount of the deposited Pt NPs was monitored by a quartz crystal oscillator embedded in the electron-beam evaporation equipment as a thickness of 2 and 5 nm (hereafter referred to as Pt/PMMA/SWNT). For comparison, SWNTs with only a PMMA coating or Pt NP decoration were also fabricated (hereafter referred to as PMMA/SWNT and Pt/SWNT, respectively). A schematic view of the hybrid sensor and details of the fabricated gas sensor are shown in Fig. 1 and Table 1, respectively.

### 2.2. Characterization techniques

The morphologies of the pristine SWNTs and PMMA/SWNTs were characterized by field emission scanning electron microscopy (FESEM; JEOL JSM-7800F). The FESEM observation was carried out in a high vacuum mode with a base pressure of approximately $9 \times 10^{-5}$ Pa and an acceleration voltage of 1 kV without any surface treatment with metallic materials. The elemental composition of Pt/PMMA/SWNT was studied by FESEM equipped with an energy dispersive X-ray spectrometer (EDS; OXFORD). Transmission electron microscopy (TEM; JEOL JE-2010) was employed to characterize the nanostructure of the Pt/SWNTs. The carbon structure, purity and crystallinity were analyzed by Raman spectroscopy (Thermo SCIENTIFIC DXR) with an Ar ion laser wavelength of 532 nm (2.33 eV). The crystal structure was characterized by X-ray diffraction (XRD; Rigaku TTRAX II) using Cu Kα with a wavelength of 1.54 Å at a scan rate of 1 °/min. The functional group of PMMA was characterized by Fourier transform infrared spectroscopy (FTIR; Perkin Elmer, Spectrum One). The FTIR sample was prepared by mixing SWNTs powder with potassium bromide (KBr) and pressing in a pellet form. Then, the prepared pellet was coated and decorated with PMMA and Pt NPs, respectively. Typical FTIR spectra in an absorbance mode were scanned in a wavenumber range of 500–4000 $cm^{-1}$.

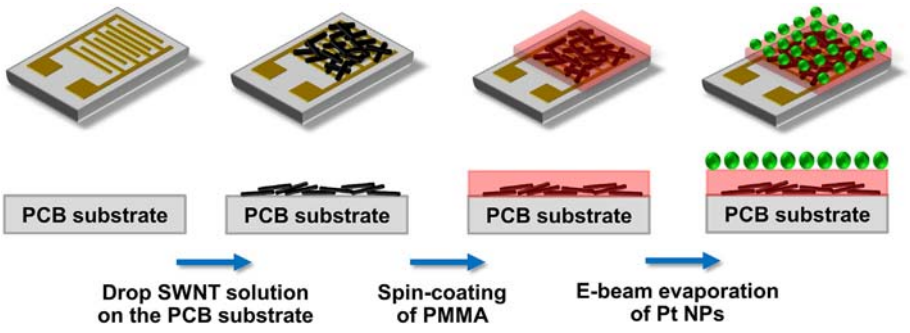


**Fig. 1.** Schematic view of hybrid sensor.