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Selective detection of chlorine at room temperature utilizing single-walled carbon nanotubes functionalized with platinum nanoparticles synthesized via ultraviolet irradiation

Sun-Woo Choi[a,c], Byung-Moon Kim[b], Sang-Hyub Oh[b], Young Tae Byun[a,*]

[a] Sensor System Research Center, Korea Institute of Science and Technology (KIST), 5 Hwarangro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea
[b] Center of Gas Analysis, Korea Research Institute of Standards and Science (KRISS), 267 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea
[c] Department of Materials and Metallurgical Engineering, Kangwon National University, 346 Joongang-ro, Samcheok, Gangwon-do 25913, Republic of Korea

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ABSTRACT

In this study, photoreduction by an ultraviolet (UV) irradiation method was applied to synthesizing platinum (Pt) nanoparticles into networked single-walled carbon nanotubes (SWCNTs). To investigate the growth behaviour of Pt nanoparticles, we systematically controlled the UV irradiation intensity and exposure time. These processing factors significantly influenced the formation behaviour of Pt nanoparticles regarding diameter and density. Utilizing the photoreduction process, the sidewalls of SWCNTs were uniformly functionalized with Pt nanoparticles synthesized under optimal UV conditions. For application as practical chlorine (Cl_2) sensors, the sensing performances of Pt nanoparticle-functionalized SWCNTs for Cl_2 were compared against the injection of other gases such as nitrogen dioxide, ammonia and carbon monoxide. The results indicate that UV irradiation is an effective way to functionalize the sidewalls of SWCNTs with catalytic Pt nanoparticles. In addition, the Cl_2 selectivity and response of SWCNT-based gas sensors were enhanced by functionalization with catalytic Pt nanoparticles.

1. Introduction

The Cl_2 gas is a major toxic pollutant at room temperature and generally used in waste water treatment, pharmaceutical production, pesticide, and paper manufacture technologies [1,2]. The threshold concentration for detection of Cl_2 by the human nose ranges from 0.1 to 0.3 ppm, whereas the exposure limit of Cl_2 recommended by US National Institute for Occupational Safety and Health (NIOSH) is 0.5 ppm [3]. Therefore, development of Cl_2 sensors, which is highly sensitive and selective, is necessary for detecting sub-ppm Cl_2 molecules.

Chemiresistive gas sensors based on semiconductors have attracted increasing attention because of their low power consumption, simple in operation and light weight compared to classical analytical instruments for the detection of hazardous, flammable, poisonous and toxic gases in diverse fields such as those related to the environment, civil life, security industries and health care [4,5]. In particular, the detection and monitoring of far-ranging gases and vapours are essential to applications of chemiresistive gas sensors. Various sensing materials used in chemiresistive gas sensors, including semiconducting metal oxides, polymers, and carbon nanotubes (CNTs), have been demonstrated for gas sensing applications [6–11].

Among semiconductor-based chemiresistive gas sensors, including metal oxides and CNTs, CNT-based sensors offered advantageous properties such as their low cost, small size, simple fabrication, and good compatibility with electronic circuits [12,13]. Accordingly, in the past decade, various types of CNT-based sensors have been developed mostly by employing different structures of CNTs: single-walled (SWCNTs), double-walled (DWCNTs), and multi-walled CNTs (MWCNTs) [14–17].

In spite of these efforts, CNT-based chemiresistive gas sensors have shown limited performance in gas response and response/recovery time due to weak interactions between the CNT-based materials and the gas molecules [17]. Therefore, improving these properties in CNT-based materials is necessary for their practical application in gas sensing.

To improve the interaction between the CNTs and some certain gas molecules, several functionalization techniques have been employed to functionalize metallic catalysts such as Pd, Ag, and Au,

* Corresponding author.
E-mail address: byt427@kist.re.kr (Y.T. Byun).

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however, at the expense of high-cost and non-uniform functionalization. Dai et al. [18] used Pd nanoparticle to modify SWCNTs for H_2 detection at room temperature, which exhibited significant response to H_2 (2 at 40 ppm). In addition, Abdelhalim et al. [19] reported that the NH_3 sensing capability of CNT-based sensors could be improved by decorating them with Ag and Au nanoparticles. As a result, a number of research groups have attempted to functionalize the sidewall of CNT-based materials with nano-sized catalytic metal nanoparticles using physical vapour deposition methods such as electron-beam evaporation deposition or sputtering techniques [20,21]. However, such physical modification of CNT-based sensors resulted in increasing device costs, the need for special instrumentation, and additional heat-treatment processes. In addition, the above-mentioned sensors exhibited poor sensing performance as a result of non-uniform dispersion of the metal nanoparticles owing to the chemical inertness of the CNTs [22].

To address the existing issues such as non-uniform dispersion, random control of metal ionization degrees and high-temperature process, UV irradiation can provide an alternative method. Although the incorporation of metallic catalysts into CNT-based sensors to improve the interaction between the carbon-based materials and the gas molecules is well-known, to our knowledge, no study has been carried out on the functionalization of sidewalls of SWCNTs with Pt nanoparticles via UV irradiation. Among the various methods for synthesis of metallic nanoparticles, UV irradiation has substantial advantages compared to conventional chemical technique: (1) The metal ions can be easily reduced to the metal species without using excessive reducing agents. (2) The neutral metal atoms uniformly generated in the solution. (3) The process performed at room temperature.

In this study, we report the introduction of UV irradiation as a room-temperature, uniform, controlled functionalization method for various CNT surfaces to enhance the gas interaction and thus the sensor response. We fabricated the room temperature response of SWCNT-based sensors, chemically functionalized by Pt nanoparticles, to chlorine (Cl_2). For practical application of Cl_2 sensors, the sensing characteristic of Pt-functionalized SWCNTs for nitrogen dioxide (NO_2), ammonia (NH_3), and carbon monoxide (CO) was also investigated. An exceptionally high response and selectivity to Cl_2 were obtained for the Pt-functionalized SWCNTs. Our experimental results exhibit a simple method of fabricating a sensitive, selective, and reversible gas sensor with improved Cl_2 sensing at room temperature. Furthermore, we propose a mechanism for the enhanced Cl_2 sensing characteristic based on the catalytic role of Pt nanoparticles.

2. Experimental

2.1. Synthesis of Pt nanoparticles by UV irradiation

For the synthesis of Pt nanoparticles by UV irradiation, precursor solutions were prepared. Briefly, 0.05 g of chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}H_2O$, Sigma-Aldrich Corp.) was dissolved in 1 mL of methanol (J.T. Baker). Then, 1 mL of the methanol solution was added to 49 mL of a methanol–deionized (DI) water mixture (90 vol.% CH_3OH–10 vol.% DI water). The prepared solutions were stirred for 4 h, after which they were irradiated with a UV lamp (VILBER, VL–4.LC) under ambient air at room temperature (at 25 °C).

To systematically investigate the growth behaviour of Pt nanoparticles by UV irradiation, the processing parameters (i.e. UV irradiation conditions), including the UV intensity and irradiation time, were varied while other conditions were fixed. Si wafers and copper grids were used to collect the Pt nanoparticles reduced in the mixed solutions. The UV irradiation conditions used in this experiment were as follows: irradiation intensity: 0.063–0.769 mW/cm^2 for 5 min; irradiation time: 5–60 min at 0.769 mW/cm^2.

2.2. Preparation of Pt-functionalized SWCNT composites

The Pt-functionalized SWCNT composites were synthesized utilizing spray method and successive UV irradiation technique. For preparation of a SWCNT suspension, 1 mg of SWCNTs with diameters in the range of 1.2–1.7 nm and lengths of 100 nm–4 μm was purchased from NanoIntergris and then uniformly dispersed in 50 mL of 1,2–dichlorobenzene ($C_6H_4Cl_2$, Sigma-Aldrich Corp.) by ultrasonication at room temperature for 4 h. Subsequently, Si substrates with a grown 300 nm-thick SiO_2 layer were prepared using a typical cleaning process that was described in our previous report [11]. In order to form networked SWCNTs, 4 mL of the SWCNT suspension was sprayed onto the SiO_2/Si substrate using an air spray gun equipped with a 0.18 mm nozzle. The networked SWCNTs successfully adsorbed onto the SiO_2/Si substrate that was placed on a hot plate heated to 180 °C. To investigate contact condition between SiO_2/Si substrate and SWCNTs depending on adsorption methods (drop casting and spray), we have measured the resistances of the electrodes deposited on the SWCNTs. As shown in Fig. S1, the resistance of electrode deposited on SWCNTs using the drop casting method is about 3 orders of magnitude lower than that of the SWCNTs using the spray method. It can be speculated that the number of junctions between the SWCNTs has influenced considerably on the resistance modulation of the working electrodes. For the functionalization of the sidewalls of SWCNTs with catalytic Pt nanoparticles, the fabricated networked SWCNTs were immersed into a Pt precursor solution (6 mL of a mixed solution). The solution was then irradiated with a 254 nm wavelength UV lamp, schematically depicted in Fig. 1. After UV irradiation, the sample was removed from the Pt precursor solution and then annealed at 300 °C for 1 h in ambient argon (Ar) to remove the remaining solvent.

2.3. Characterization of Pt-functionalized SWCNT composites

To analyze the microstructure and phase of synthesized Pt nanoparticles, field-emission scanning electron microscopy (FE–SEM, FEI Nova–SEM), transmission electron microscopy (TEM, JEOL TEM 2100F) equipped with an energy-dispersive X-ray spectrometer (EDS), and X–ray diffraction (XRD, Rigaku D/max–2500 PC) were performed. The elemental composition analysis was performed by X-ray photoelectron spectroscopy (XPS, Thermo K–Alpha) with focused monochromatized Al Kα (1486.6 eV) radiation.

2.4. Sensor measurements

The sensing characteristic of the Pt-functionalized SWCNTs for diverse gases (Cl_2, NO_2, CO, and NH_3) was measured in a quartz chamber at room temperature using a home-made sensing system. For sensing measurement, an electrode was prepared by sequential deposition of Ni (50 nm thickness) and Au (200 nm thickness) on the prepared samples with an interdigitated electrode (IDE) mask consisting of 4 fingers utilizing a sputtering technique. The 50 nm–thick Ni layer was used to enable good adhesion between the Au layer and substrate. For the IDE mask, each electrode was 6.85 mm long and 0.5 mm wide and the spacing between the neighbouring electrodes was 150 μm. However, in order to obtain the best sensing performance, a more optimized process for making the electrode is required. Because deposition of the electrode metal layer of 250 nm thickness on a porous structure such as SWCNTs mat is not likely to provide high quality contact. The gas concentrations were controlled at a ratio of calibrated target gas (buffered with dry air) to