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Full Length Article

The effect of platinum precursor concentrations on chlorine sensing characteristics of platinum nanoparticles–loaded single walled carbon nanotubes

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ABSTRACT

The correlation between platinum (Pt) functionalization and chlorine (Cl_2) sensing capability in single-walled carbon nanotubes (SWCNTs) was investigated. Utilizing a photoreduction technique via ultraviolet (UV) irradiation, the Pt nanoparticles (NPs) with various diameters of 7–80 nm, which were controlled by Pt precursor concentrations, were successfully functionalized on the sidewalls of SWCNTs. The discrete Pt NP–loaded SWCNTs exhibited significantly enhanced response value ($-(\Delta R/R_0) \times 100 = 33.8\%$) for 1 ppm Cl_2 at room temperature (25 °C) compared with that (no response) of pure SWCNTs. On the other hand, in case of continuous Pt NP–loaded SWCNTs, Cl_2 sensing capabilities were significantly degraded. The Cl_2 sensing capabilities of fabricated sensors tended to correlate with geometric configurations of the catalytic Pt NPs on the sidewalls of SWCNTs, due to differences in the electron pathway.

1. Introduction

Semiconducting carbon–based nanomaterials, such as carbon nanotubes (CNTs), graphene, graphene oxide (GO), and reduced–graphene oxide (RGO), have attracted considerable attention as promising sensing materials due to their excellent gas response at room temperature. In particular, its outstanding electrical, mechanical and thermal properties and structural advantages such as a high surface–to–volume ratio and a high specific surface area can be applied to gas sensor applications through the adsorption and desorption of gas species. Thus, gas sensors, utilizing the carbon–based nanomaterials, have recently been demonstrated for detecting NO_2 [1], NH_3 [2], CO [3], and VOCs (Volatile Organic Compounds) [4,5]. However, poor selectivity and irreversible recovery of carbon-based nanomaterials are still critical drawbacks for realization of practical and reliable gas sensors.

In order to overcome above–mentioned drawbacks, surface functionalization (or engineering) with nano–sized metal/metal oxide catalysts has been used and then demonstrated that poor selectivity and irreversible recovery can be improved with gas response. Although, metal/metal oxide catalysts, including Au [6], Pt [7], Pd [8], SnO_2 [9], Co_3O_4 [10], and CuO [11], have been known to drastically enhance the sensing capabilities of carbon–based nanomaterials, to the best of our knowledge, the effect of the additive concentrations and morphology of metal/metal oxide catalysts on gas sensing capabilities has rarely been investigated [12,13]. In particular, the carbon–based nanomaterials functionalized with Au, Ru, Ag, Pt, and bi–metallic nanoparticles have been extensively studied for various applications in electrochemical sensors and electrocatalysts for fuel cells as well chemical gas sensors [14–24]. In this respect, systematic investigations on the optimization and synthesis strategies of catalytic metal nanoparticles are essential for expediting the practical realization of carbon–based nanomaterials to chemical gas sensors.

In this study, we functionalized the Pt nanoparticles (NPs) with various diameters onto the sidewalls of single–walled CNTs (SWCNTs) utilizing a photoreduction technique and investigated the role of additive concentration, the size and the geometric configuration of Pt NPs in Cl_2–sensing response of SWCNT–based sensors. For comparison of the enhanced sensing response, pure, discrete Pt NPs–loaded, and continuous Pt NPs–loaded SWCNT sensors were systematically tested for 1 ppm Cl_2 at room temperature. This contribution focused on not only the Cl_2–sensing mechanism of Pt

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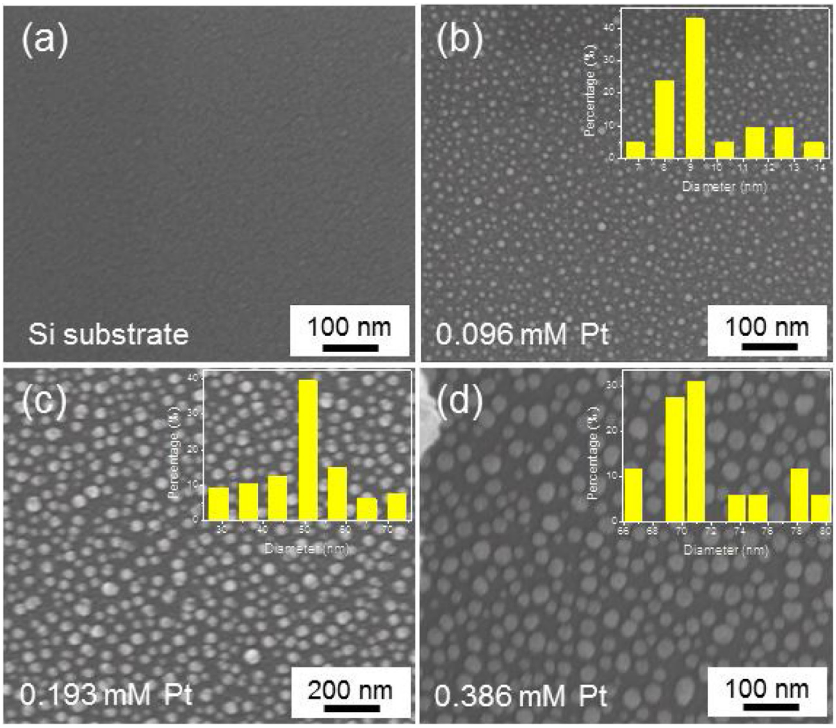

Fig. 1. Typical FE–SEM images and histograms of Pt NPs synthesized with different concentrations of Pt precursor: (a) bare Si substrate, (b) 0.096, (c) 0.193, and (d) 0.386 mM $H_2PtCl_6{\cdot}H_2O$.

NPs–loaded SWCNTs but also the effect of the geometric configuration of Pt NPs on Cl_2 sensing response.

2. Experimental section

SWCNTs with 1.2–1.7 nm diameters and 100 nm–4 μm lengths were purchased from NanoIntergris Inc. For synthesis of SWCNTs networks, a 0.02 mg/mL of suspension, 1 mg of SWCNTs dispersed in 50 mL of 1,2–dichlorobenzene ($C_6H_4Cl_2$, Sigma–Aldrich Co., Ltd., USA), was prepared by ultrasonic treatment at room temperature for 4 h. A SiO_2 (300 nm)-deposited Si substrate was placed on a hot plate heated to 180 °C. The SWCNTs were uniformly adsorbed on the SiO_2/Si substrate by a spray method utilizing an air spray gun equipped with a 0.18 mm nozzle. In order to synthesize Pt NPs of various sizes and distributions, precursor solutions were prepared using the following process. First, Pt precursors ($H_2PtCl_6{\cdot}H_2O$, Sigma–Aldrich Co., Ltd., USA) of three different molar concentrations (0.096, 0.193 and 0.386 mM) were dissolved in 1 mL of methanol (CH_3OH, Avantor Performance Materials, Inc., USA). Second, the methanol solutions were mixed with a 49 mL of methanol–deionized (DI) water mixture (CH_3OH: DI water = 90: 10 by vol.%) and stirred for 4 h. Third, the SWCNT–sprayed substrates were immersed into each precursor solution. Finally, in order to load Pt nanoparticles on the sidewalls of SWCNTs, each of the solutions were irradiated with a UV lamp (VILBER, VL–4.LC) under ambient air at room temperature. The UV irradiation conditions used in this paper were maintained to an intensity of 0.769 mW/cm^2 and time of 5 min. The fabricated samples were heat–treated at 300 °C to eliminate some residues such as H_2O and organic contents.

The sensing capabilities of pure and Pt NP–loaded SWCNTs were tested in a quartz chamber at room temperature (25 °C) using a home–made sensing system. To investigate the sensing capabilities, an interdigitated electrode (IDEs, electrode width: 0.5 mm; gap between electrodes: 0.15 mm) with four fingers was fabricated by sequential deposition of Ni (50 nm thickness) and Au (200 nm thickness) on the SWCNT–sprayed substrate (size: 8 × 8 mm^2). For good adhesion between the Au film and the substrate, the 50 nm–thick Ni film was used. All sensing measurements were performed in a specially designed quartz tube at room temperature while the gas concentrations (a ratio of calibrated target gas to dry air balance gas) were controlled by utilizing accurate mass flow controllers. In addition, to avoid any possible variation, a total flow rate was kept constant (500 sccm) during sensing measurements. The sensing characteristics of the Pt NP−loaded SWCNT sensors for various gases (oxidizing gases: NO_2 and Cl_2, reducing gases: NH_3 and CO) were investigated at room temperature using a home−made gas dilution and sensing system. The gas response to oxidizing gases was determined as the $-(\Delta R/R_0) \times 100$, where R_0 is the initial resistance before injection of a target gas and ΔR is the resistance variation during the target gas exposure. In case of reducing gases, $(\Delta R/R_0) \times 100$ was used to compare the gas response with oxidizing gases.

The morphology and phase analysis of Pt NPs and Pt NP–loaded SWCNTs were performed by utilizing field emission scanning electron microscopy (FE–SEM, FEI Nova–SEM), transmission electron microscopy (TEM, JEOL TEM 2100F), and X–ray diffraction (XRD, Rigaku D/max–2500 PC). To estimate an average diameter of Pt NPs synthesized at different Pt precursor concentrations, ImageJ software was utilized. The chemical state of Pt NPs was also analysed by X–ray photoelectron spectroscopy (XPS, Thermo K–Alpha) with focused monochromatized Al Kα (1486.6 eV) radiation.

3. Results and discussion

To investigate the effect of Pt precursor concentration on the average diameter, Pt NPs were synthesized on the Si substrate at the identical UV irradiation condition (UV intensity: 0.769 mW/cm^2; UV irradiation time: 5 min). Fig. 1(b)–(d) exhibit the typical FE–SEM images synthesized at the different Pt precursor concentrations (0.096, 0.193 and 0.386 mM), showing that the diameters of Pt NPs increases with increasing Pt precursor concentration. The average