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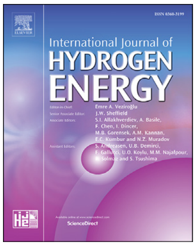

Aerogel sheet of carbon nanotubes decorated with palladium nanoparticles for hydrogen gas sensing

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ABSTRACT

In the development of hydrogen sensors, it is required to meet the demands of both high sensor performance as well as the ease of fabrication for mass production. For this purpose we proposed a chemiresistive hydrogen sensors based on an aerogel sheet of carbon nanotubes decorated with palladium nanoparticles (CNT/Pd sheet). The fabrication process is straightforward that a dry-spun CNT aerogel sheet is suspended between concentric electrodes followed by depositing Pd nanoparticles on CNT sheets by thermal evaporation. The present CNT/Pd sheet sensors can detect hydrogen at concentrations as low as 2 ppm at room temperature with a detection range from 2 to 1000 ppm. The aerogel nature of CNT/Pd sheet contributes to low detection limit and broad detection range of the CNT/Pd sensor. Relations between hydrogen concentration and sensor response and response time, and the effects of temperature on sensor performance were investigated.

Introduction

Hydrogen is being widely utilized as an energy source, for example, in vehicles, aero planes, fuel cells, and as a general fuel [1–3]. Despite its high calorific value per unit weight, the calorific value of hydrogen by volume is only one third that of natural gas, and thus, it is often stored and utilized at high pressure or as liquid hydrogen or metal hydrides [4–6]. However, hydrogen reacts with oxygen and gas mixtures can spontaneously explode when the concentration of H_2 in air exceeds 4%. For this reason, hydrogen sensing and related safety systems must be widely adopted during the production, storage, transportation, usage of hydrogen.

In the development of high performance hydrogen sensors, the sensors based on the chemiresistive method have attracted much attention due to the advantages of high sensitivity, real-time detection and low power consumption. Carbon nanotubes (CNTs) decorated with palladium (Pd) nanoparticles have been widely studied as hydrogen responsive elements for chemiresistive sensing. Palladium exhibits high specific solubility for H_2 by forming palladium hydrides and high gas selectivity [7–9]. CNTs and their assemblies have been used as a pathway for transferring electrical changes resulting from the reaction of Pd with hydrogen. In addition to considerations of the reactivity of Pd with CNT interfaces [10–12], theoretical studies have revealed the mechanism of atomic and molecular hydrogen adsorption onto Pd surfaces [13–16]. Based on these efforts, a variety of high performance hydrogen sensors have been demonstrated [17–25].

In this study, we propose a fabrication process for hydrogen sensors incorporating a CNT sheet decorated with Pd nanoparticles (CNT/Pd sheet) that provides high sensor performance as well as mass-production suitability. Unlike

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the regular side-by-side electrode structure in typical chemiresistive sensors, a concentric electrode design was employed to facilitate fabrication of the sensor platform. A dry-spun CNT aerogel sheet was simply suspended between these concentric electrodes. The sensor fabrication was completed by depositing Pd nanoparticles on CNT sheets by thermal evaporation. The fabricated CNT/Pd sensors detected hydrogen at concentrations as low as 2 ppm at room temperature with a detection range from 2 to 1000 ppm. The sensor responses and response times at different hydrogen concentrations and sensor performance at different temperatures were also investigated.

Fabrication of CNT/Pd sheet sensors

The sensor platform was fabricated using a standard lift-off process with a 0.5 μm thick Au layer on thermally grown silicon dioxide. A photograph and a conceptual diagram of a sensor platform is shown in Fig. 1(a) and (b), respectively. A concentric electrode design was employed to facilitate fabrication of the sensor platform, which is comprised of an inner electrode (island electrode, IE) enclosed by an outer electrode (enclosing electrode, EE). The electrode gap between IE and EE is 30 μm.

Fig. 1(c)–(e) shows the sensor fabrication procedure including CNT sheet lamination and subsequent deposition of a Pd film on CNT sheets. CNT aerogel sheets were drawn from a sidewall of a carbon multi-wall nanotube (MWNT) forest using a dry-state draw process, which typically produced a sheet areal density of ~2 μg/cm^2 and a sheet thickness of ~20 μm [26,27]. To form the CNT/Pd sheet sensing element on the sensor platform, we simply placed cross-plied CNT aerogel sheets over the IE and EE electrodes (Fig. 1(c) and (d)). A 10 nm thick Pd film was then deposited on the sheet by thermal evaporation (Fig. 1(e)). During the thermal evaporation process, adsorbed Pd atoms nucleated and grew into individual nanoparticles on CNT sheet surface due to the greater cohesive bonds between Pd atoms than adhesive bonds between Pd atoms and CNT surface [28–30]. It is noteworthy that the devised process has substantial advantages for production-scale processes and does not need any cumbersome process to pattern CNTs and Pd nanoparticles.

Scanning electron microscopy (SEM) was used to observe the morphologies of CNT/Pd sheets suspended on electrodes. As shown in Fig. 2(a) and (b), cross-plied CNT/Pd sheet were well-suspended and entirely covered the electrical channel area between IE and EE. Transmission electron microscopy (TEM) revealed that Pd nanoparticles of diameter 3–10 nm were produced on CNT sheet (Fig. 2(c)). Pd nanoparticles were uniformly formed on the surfaces of individual CNT inside the sheet due to the diffusion of Pd vapors into CNT aerogel sheet during the thermal evaporation.

Performance evaluation of CNT/Pd sheet sensors

Sensor performance for hydrogen detection was evaluated in terms of sensor response and response time. Sensor response is defined as the percentage change in resistance when the sensor is exposed to hydrogen ($\Delta R/R_0 \times 100\%$), where ΔR is the resistance change and R_0 is initial sensor resistance. Response time (τ_{res}) and recovery time (τ_{rec}) are defined as the time required for a sensor to increase the resistance change to 1-1/e (~63.2%) of its maximum resistance change after the sensor is exposed to hydrogen [22,23], and the time required to decrease the resistance change to 1/e (~36.8%) of the maximum resistance change for the recovery of the sensor, respectively.

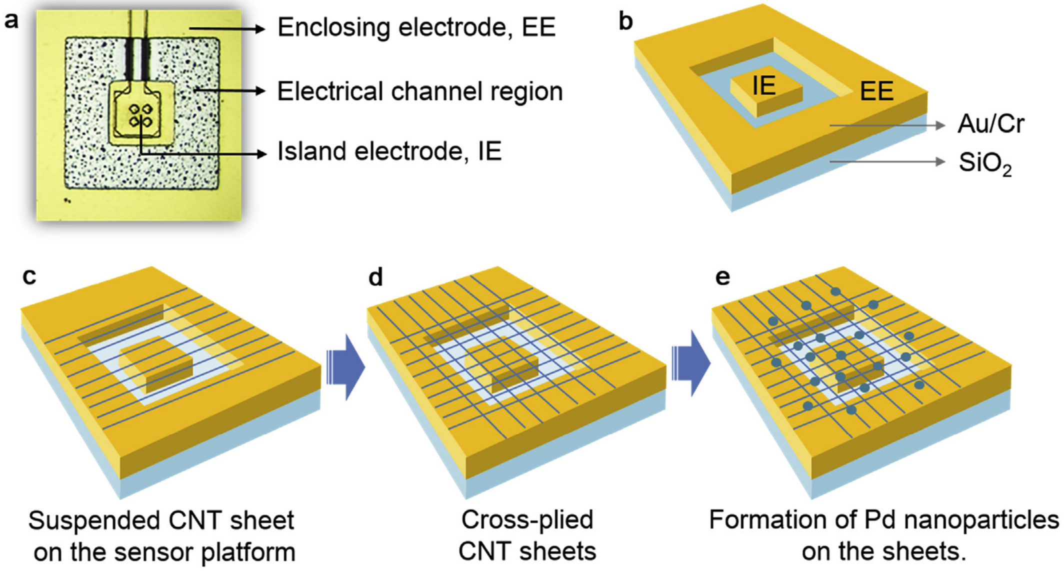

Fig. 1 – A photograph and a conceptual diagram of a sensor platform is shown in Figure 1(a) and (b), respectively. The sensor platform adopts a concentric electrode comprised of an inner electrode enclosed by an outer electrode. Schematic of the fabrication procedure is shown through (c) to (e). (c) A CNT sheet was suspended on the sensor platform, (d) cross-plying of CNT sheets and (e) deposition of Pd film on the sheets.