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General

Dielectrophoresis of graphene oxide nanostructures for hydrogen gas sensor at room temperature

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ABSTRACT

Hydrogen gas sensors based on graphene oxide (GO) nanostructures have been fabricated using ac dielectrophoresis (DEP) process. The GO nanostructures synthesized by an improved Hummer's method were first characterized by atomic force microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. GO nanostructures were assembled into gold electrodes using DEP process by varying parameters such as frequency, peak-to-peak voltage (V_{pp}), and processing time (t). The devices were investigated by scanning electron microscopy, current-voltage measurement, and hydrogen sensing experiment at room temperature. It was found that the optimum DEP parameters that manipulates GO nanostructures in precise manner for hydrogen gas sensing were V_{pp} = 10 V, frequency = 500 kHz, and t = 30 s. The optimized device was proved to be an effective and better hydrogen gas sensor over a typical drop-dried device with a good sensing response of 5%, fast response time (<90 s), and fast recovery time (<60 s) for 100 ppm hydrogen gas concentration at room temperature.

1. Introduction

Hydrogen gas is one of the most promising, clean, and renewable energy sources and has the potential to meet the energy needs of tomorrow. Hydrogen gas is extensively used as a clean energy carrier for fuel cells, power generation, scientific research, methanol industries, and in fertilizer plants [1,2]. However, hydrogen is a colorless, odorless, and tasteless gas. As a result, it is considered dangerous owing to its invisibility and flammability. In addition, there is a high risk of explosions when hydrogen gas at concentrations of above 4% is mixed with air. Moreover, physical hazards remain the most significant concern when working with hydrogen gas. Therefore, the ability to measure the properties of or sense hydrogen gas is important for its safe storage, transportation, and the advancement of fuel cell technology.

Extensive research efforts have been made to develop a hydrogen gas sensor with high sensitivity and a fast response and recovery time. Presently, the use of nanostructure materials in gas sensing applications has attracted considerable interest owing to the unique and outstanding properties of these materials, such as a maximum surface-to-volume ratio that can help to develop gas sensors with exceptional performances. Many hydrogen sensors based on metal and metal oxide nanostructures have been studied so far [3–6]. However, they require elevated temperatures in during practical use, thus posing an operational hazard.

Recently carbon nanotubes (CNTs) were proposed to be a promising sensing element for sensing various gases at room temperature. Although CNTs have been proven to be a good gas sensing material, pure CNTs exhibit no response to H_2 due to their weak binding energy [7]. When CNTs are attached to precious metal nanostructures such as Pt or Pd, H_2 sensing at room temperature becomes possible because the metals act as catalysts for the adsorption of H_2 [8,9]. However, the use of the expensive precious metals is an obstacle to reducing the manufacturing cost of hydrogen gas sensors.

In the past few years, graphene has attracted considerable attention for gas sensing applications owing to its sp^2-hybridized 2D hexagonal honeycomb structure [10–12]. However, even sensors that use graphene require platinum group metals for hydrogen sensing. Very recently, researchers attempted the use of reduced graphene oxide (rGO) instead of graphene for sensing applications because it has controllable surface defect density, which modulates the sensitivity and specificity of the sensor [13–15]. However, in sensors that use rGO instead of graphene, an additional thermal

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or chemical process is required for the reduction, which increases the manufacturing cost. Wang et al. attempted to use graphene oxide (GO) as a hydrogen-sensing element with the drop coating technique [14]. However, their sensors exhibited very poor reproducibility, in addition to very low sensitivities and long recovery times. The drop coating technique is the preferred method for gas sensor researchers because the process is very simple and saves time. However, the quality control of the process is problematic.

Dielectrophoresis (DEP) has become increasingly popular in recent years because this technique has the ability to position nanostructures precisely on a substrate. The use of DEP alignment of various materials, such as Au nanocolloids, in addition to biomaterials including DNA, carbon nanotubes, and semiconducting nanowires, has been widely exploited for practical applications in the fields of nanotechnology, in addition to devices used in biotechnology such as field-effect transistors, molecular electronics, biosensors, and gas sensors, respectively [16–23]. The merits of this technique are that it offers the precise positioning of nanomaterials, a high surface-to-volume ratio of subsequent nano-networks, and excellent linking of the electrodes and the nano-network. In this work, we report on GO hydrogen gas sensors fabricated by the DEP technique for the first time. The GO nanostructure was assembled into microgap electrodes by controlling the DEP parameters, such as the applied frequency, applied voltage, and processing time.

2. Experimental details

GO nanostructures were synthesized using a modified Hummer's method. In this method, four grams of graphite flakes were added to a 250 ml round-bottom flask containing 120 ml of H_2SO_4 that was stirred for 1 h. $KMnO_4$ aqueous solution was added to the mixture every 20 min while stirring. The mixture was slowly heated to 40 °C and maintained at that temperature for 5 h to oxidize the graphite. Subsequently, 150 ml of deionized (DI) water was added to the mixture. Next, 17 ml of H_2O_2 solution was added to the mixture while stirring it for 30 min. The mixture was then maintained at the same temperature for 24 h, after which it was centrifuged. The resultant mixture was enclosed in a dialysis tube washed with ultrapure DI water several times to obtain a pH level of 5. Finally, the GO was dried in a freeze dryer at 60 °C for 48 h. Before the DEP process, the GO solution was subjected to ultra-sonication for 24 h to reduce the size of GO flakes. The filtration was treated on the solution after the ultra-sonication process.

An X-ray diffraction (XRD) study was carried out using a PANalytical Xpert Pro X-ray diffraction meter with nickel-filtered Cu K_α radiation as the X-ray source. The samples were scanned in steps of 0.02° in the 2θ range of 5–20°. The chemical bonding characteristics of the GO nanostructures were examined using X-ray photoelectron spectroscopy (XPS) (ESCA 2000, VG Microtech: U.K.) using twin anode X-ray sources K_α (1,486.6 eV)/Mg K_α (1253.6 eV) in a vacuum of 10^{-9} Torr. Raman spectra were acquired using a WITec Raman microscope with a 532 nm laser. The sensing properties and performance of the device were checked in the vacuum chamber using flowing hydrogen gas with different concentrations of 100, 200, 500, 800, and 1000 ppm. The sensing measurement requires three consecutive steps (i) clean air flow to record initial value of the conductance, (ii) the target gas has been introduced into a mixing chamber with clean air at optimized concentrations, (iii) flow of mixed gas to register a sensing signal, and (iv) clean air flow for sensing recovery. Current–voltage (*I–V*) characteristics of the GO nanostructures between the Au electrodes were investigated using the *I–V* measurement system (Keithley, Model: 4200-FCS).

In this paper, we report a GO hydrogen gas sensor fabricated by the DEP technique. The GO nanostructure was assembled into microgap electrodes by controlling the DEP parameters, such as the applied frequency, applied voltage, and processing time. Fig. 1a,b and c show the schematic representation of the experimental setup used for applying the DEP process before, during, and after DEP respectively. Fig. 1d shows a finite element method (FEM) simulated electric field profile of GO nanostructures on Si/SiO_2 substrates, where spatial electric field increases from top to bottom of the solution drop resulting in the DEP force as shown by red arrows in Fig. 1b. Fig. 2a,b shows the optical microscope image of the 4 μm gap Ti/Au (10/100 nm) electrode fabricated on a Si/SiO_2 (300 nm) substrate using photolithography and lift-off techniques. A solution of 0.1 μl was dripped into the Au electrodes using a micropipette, and an ac voltage using functional generator (Tektronix AFG 3102) connected with an oscilloscope (Tektronix TDS 3052C) was applied to begin the DEP process. This field gradient is responsible for pulling the GO nanostructures from the solution towards the SiO_2 plane bounded by the electrodes, thus resulting in the fine GO-assembly between the electrode pair. As this DEP

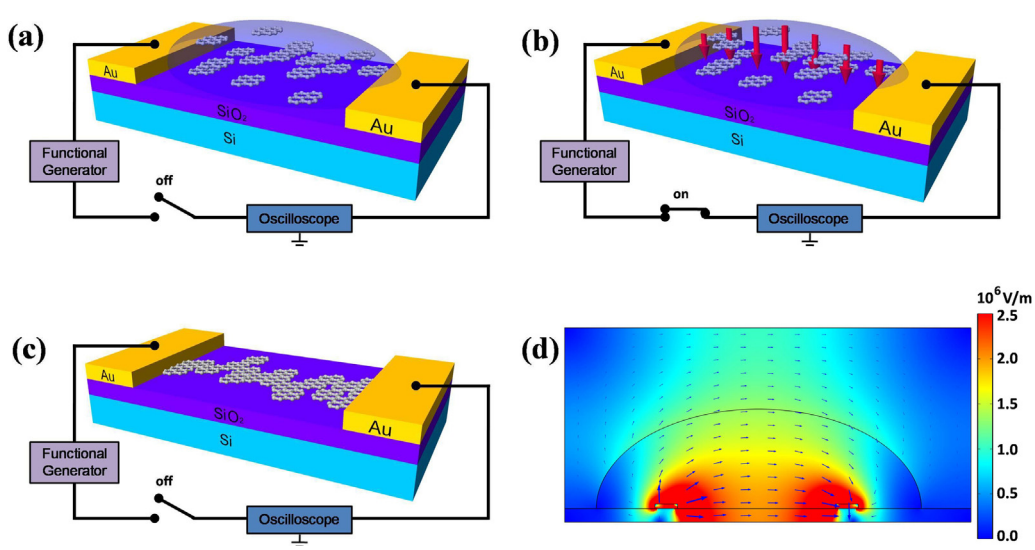

Fig. 1. Schematic representation of the setup used for the DEP of GO nanostructures in a microgap of a Au electrode (a) before, (b) during, (c) after DEP. The bold red arrows in (b) shows the direction of the DEP force acting on the suspended GO nanostructrues, under the influence of which the floating nanostructures got assembled between the electrodes. (d) FEM simulated electric field between a pair of coplanar Au electrodes with a solution drop showing the variation in the electric field intensity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).