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A practical carbon dioxide gas sensor using room-temperature hydrogen plasma reduced graphene oxide

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ABSTRACT

We report on the development of a carbon dioxide gas sensor from the room-temperature reduction of graphene oxide via hydrogen plasma. The hydrogen plasma contains radicals and atoms which give dissociation energies for oxygen functional groups, which is capable of reducing the graphene oxide. The sample morphology, degree of reduction, chemical bonding and gas sensing capability were systematically studied. The effective removal of oxygen functional groups at the edges and both basal planes while restoring C=C bonds has been observed by AFM, XPS and Raman analysis. The C/O ratio increased from 0.81 to 7.9 and the resistance decreased significantly from 33 kΩ to 1.6 kΩ after the reduction process. The fabricated rGO-F20 sensor shows the highest CO_2 gas sensing response of 71% and 15% at 1500 ppm in N_2 (37% RH) and air environment (68% RH), respectively. In addition, the sensor shows a good repeatability performance with the sensing and recovery time of about 4 min when exposed to 750 and 769 ppm CO_2 concentration. The repeatability performance was measured in air environment at 68% RH without external assisted recovery. This simple, room-temperature reduction process and sensing capability, low cost fabrication process of a graphene sensor could lead to the implementation of a practical indoor air quality monitor.

1. Introduction

Since the discovery of graphene by Novoselov and Geim in 2004, immense efforts have been focused on graphene oxide (GO) [1]. This is because it is the most promising precursor to obtain mass production of graphene compared to micromechanical exfoliation and catalytic decomposition of hydrocarbons on transition metals [2–4]. Simplified Hummer's method was employed to weaken the van der Waals forces of graphite by introducing oxygen functional groups thereby promoting complete exfoliation of graphene oxide (GO) sheets in aqueous media [5]. However, the presence of oxygen functional groups on the graphene sheets reduces electron mobility typically becoming an insulator and thus removal of these functional groups to restore its conductivity is a challenging task.

Several approaches for a reduction process have been reported such as hydrazine chemical treatment [6,7], thermal reduction [8,9] and hydrogen plasma treatment [5,10–12]. The chemical approach using hydrazine is a widely used route to reduce GO, but it leads to nitrogen impurities after the reduction process and hydrazine itself is toxic [13]. A high degree of reduction was achieved using thermal reduction at elevated temperatures (1000–1100 °C) and was found to be efficient in producing graphene with a significantly high C/O ratio. However, such high temperature processing is unlikely to be practical with the fabrication techniques used for most electronic applications [13,14]. Lastly, hydrogen plasma treatment offers a unique advantage since it can be performed at low temperatures [10]. However, sputtering and bombardment effects caused from energetic species such as ions led to the formation of porous and rougher rGO, thus careful parameters need to be chosen. Since reduction by hydrogen plasma has not been extensively studied compared to other reduction techniques such as chemical or thermally reduced graphene, there are many points of interest to investigate. These include the reduction mechanism and the optoelectronic properties of reduced graphene oxide.

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Reduced graphene oxide (rGO) has a lot of potential as a platform for many applications such as gas sensing, transparent conducting electrodes, ultracapacitors and thin film transistors [14]. Recently, graphene has been demonstrated as a promising sensing material for several reasons; first, it has a unique two-dimensional carbon nanostructure which provides a large surface area per unit volume and as a result every atom at the surface may be involved in the gas interaction [6]. Second, the ease of functionalization of different materials on graphene that act as capture agents enable selectivity of a target gas [15]. Lastly, the production of graphene uses graphite, which is inexpensive and highly abundant [16]. These properties make graphene an ideal candidate for practical gas sensors for industrial, environmental, public safety and military applications.

Target gases such as nitrogen dioxide, ammonia, oxygen, carbon monoxide and hydrogen have been extensively studied [6,15,17,18]. However, carbon dioxide gas has not been studied as much as the other gases mentioned [19]. CO_2 is a colourless, odourless, and tasteless gas. It is a product of completed carbon combustion and the by-product of biological respiration. The primary source of CO_2 in indoor environment (for example, buildings and laboratories) is from respiration of the indoor occupants [20]. Normal outdoor air and indoor occupied space with good air exchange typically has a CO_2 level of 350 to 800 ppm. High CO_2 levels may indicate a problem with overcrowding or inadequate outdoor air ventilation rates. Adverse health effects from CO_2 may occur since it is an asphyxiant gas which can caused headache, fatigue, eye symptoms, nasal symptoms (sore throat) or respiratory tract symptoms (irritated nose/sinus). According to the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) Standard 62-1989, the CO_2 concentration in occupied buildings should not exceed 1000 ppm [20]. While, Building bulletin 101 (Bb101), reported that for the United Kingdom, standards for schools say that CO_2 averaged over the whole day (i.e. 9 am to 3.30 pm) should not exceed 1500 ppm [20]. Therefore, monitoring the levels of CO_2 in indoor air quality can prevent a significant impact on human health.

In this study, we focus on a room temperature GO reduction by exposing it to hydrogen plasma at various times and hydrogen flow rates. This low temperature, environmentally friendly and efficient method of removing oxygen functional groups may provide an alternative for the preparation of rGO on various substrates. We also evaluate the sensing characteristic of the rGO sample for various concentrations of carbon dioxide gas at room-temperature. However, further studies on sensor performance evaluation will require more realistic test conditions, e.g. effect of relative temperature and humidity on the CO_2 response properties or selectivity of different type of detected gases is needed.

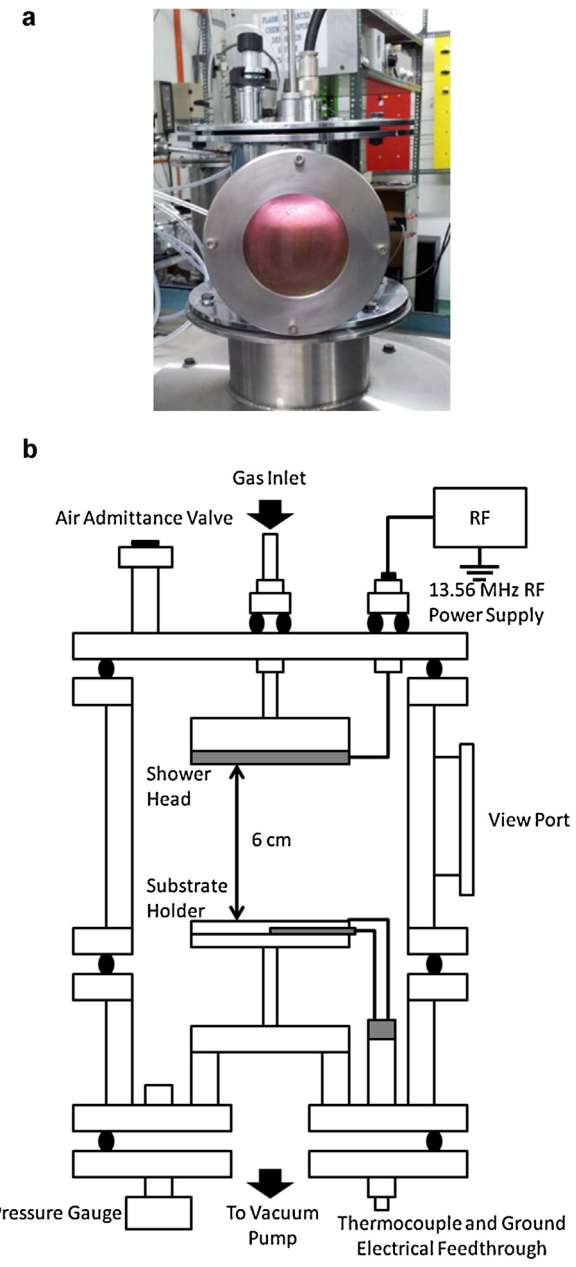

Fig. 1. (a) Photograph and (b) schematic diagram of the custom-made plasma enhanced chemical vapour deposition (PECVD) chamber used for room-temperature hydrogen plasma reduction.

2. Experimental details

2.1. Hydrogen plasma reduction

Graphene oxide (GO) was prepared from natural graphite flakes (Asbury Graphite Mills, Inc) using the simplified Hummer's method [21]. The samples were spin-coated with 1 mg/mL of GO on quartz and 300 nm thick SiO_2/Si substrates. A custom-built plasma enhanced chemical vapour deposition was employed to perform the hydrogen plasma, radical-assisted chemistry method on the samples. Next, a 13.56 MHz radio frequency generator was used to ignite the hydrogen plasma in between two metallic-parallel plate electrodes (Fig. 1) with 10 W radio-frequency power for; (Set 1) 20 and 40 s treatment time; (Set 2) 50 sccm and 20 sccm hydrogen flow rate, referred to as rGO-P20, rGO-P40, rGO-F50 and rGO-F20, respectively. For the samples in Set 1, the pressure is fixed at 0.8 mbar and 50 sccm hydrogen flow rate while varying the reduction time at 20 and 40 s. In Set 2, the reduction time was fixed at 40 s while the pressure measured is 0.65 and 0.30 mbar when fed with 50 and 20 sccm hydrogen, respectively. These parameters with separation distance and radio-frequency power were altered to reduce the sputtering and bombardment effect caused from energetic hydrogen ions that may lead to the formation of porous and rougher rGO. A thermocouple located at the substrate holder was monitored during the reduction process and the increase of temperature caused by the plasma itself was measured at around $27 \pm 1\,^{\circ}C$ (measured from longest treatment time).

2.2. Carbon dioxide gas sensor

The electrical behaviour of the graphene sensors was studied by measuring a change in resistance with various parts per million