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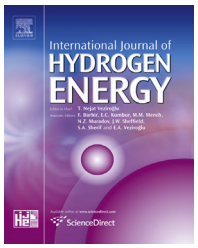

Characteristics of resistivity-type hydrogen sensing based on palladium-graphene nanocomposites

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ABSTRACT

We describe the characteristics of resistivity-type hydrogen (H_2) sensors made of palladium (Pd)-graphene nanocomposites. The Pd-graphene composite was synthesized by a simple chemical route capable of large production. Synthesis of Pd nanoparticles (PdNPs) of various sizes decorated on graphene flakes were easily controlled by varying the concentration of Pd precursors. Resistivity H_2 sensors were fabricated from these Pd-graphene composites and evaluated with various concentrations of H_2 and interfering gases at different temperatures. Characteristics for sensitivity, selectivity, response time and operating life were studied. The results from testing the Pd-graphene indicated a potential for hydrogen sensing materials at low temperature with good sensitivity and selectivity. Specifically H_2 was measurable with concentrations ranging from 1 to 1000 ppm in laboratory air, with a very low detection limit of 0.2 ppm. The response of the sensors is almost linear. The resistivity of sensors changed approximately 7% in its resistance with 1000 ppm H_2 even at room temperature. The robust mechanical properties of graphene, which supported these PdNPs, exhibit structural stability and durability in H_2 sensors for at least six months. Moreover, the advantages in this work are experimental reproducibility in synthesis Pd-graphene composite and sensor fabrication process.

1. Introduction

Graphene, a monolayer of two-dimensional (2D) atomic carbon sheets, has garnered considerable attention for its unique electrical, physical, and optical properties [1–3]. These unique properties hold promise for a wide variety of applications in field-effect transistors, ultrasensitive sensors, electrochemical devices, transparent electrodes, and novel nanocomposites [1–6]. Since the first reported graphene-based gas sensor for NO_2, NH_3, H_2O, and CO was reported by Shedin et al. [1], there have been a number of theoretical and experimental studies regarding the gas sensing properties of mechanically exfoliated graphene [1,5–7], chemical exfoliation graphene (or graphene oxide) [8], wafer-scale graphene by chemical vapor deposition (CVD) [9], and epitaxial graphene on SiC [10]. Among these synthesis methods of graphene, chemical exfoliation is superior in that it requires inexpensive raw materials and facilitates simple, large amounts of production, and easy functional graphene (from graphene oxide) [2,3,8].

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Despite the potential of graphene-based solid gas sensors, the selectivity of sensor-based graphene for specific gas/biomolecules targets for practical gas sensors requires functionalized graphene [6,11] with a noble metal catalyst [9,10,12–15], metal/metal oxide in the form of hybrid structures [16,17], or nanocomposites [18,19]. Furthermore, functionalized graphene-based sensors not only have improved the sensitivity and selectivity towards their target gases, but also exhibit sensor stability in moist environments [6]. In particular, graphene-based nanocomposites are also promising in a large number of applications including energy conversion, energy storage, catalysis, and sensing of medical and biological/gases sensing [4,20]. In nanocomposites, graphene has a high specific area to support catalysts and thus is a perfect scaffold for well dispersed, isolated, wrapping, and holding other nanomaterials with good mechanical properties [3,4,20]. Moreover, the atomic thickness of graphene provides a new pathway for molecular diffusion and charge transport, which are critical in nanocomposite-based bio/gas sensors [3].

Recently, graphene oxide (GO) and reduced graphene oxide (RGO) have been widely used for various applications including photocatalysis, bio-technology, and sensing [2–4,8,16–22]. GO is generated by oxidation of graphite and contains a wide range of functional oxygen groups such as hydroxyl and epoxy groups on the basal plane and carboxylic acid groups at the edges, which make GOs strongly hydrophilic [3,8]. The hydrophilic properties created by attaching oxygen-functional groups of GOs yield a large number of advantages with respect to compatibility in MEMS/NEMS processes, biocompatibility, and producing functional graphene [2–4,16–22]. The native oxygen-functional groups attached on GO flakes are critical for functionalized graphene with metal/metal oxide by simplified one-step [16–20,23].

For a future hydrogen-based economy, hydrogen (H_2) sensors will be a critical for safety and will be widely needed in various applications [12–14,17–19,24–31]. Among various sensing materials and noble metal catalysts for H_2 sensors, a palladium (Pd) nanostructure is a well-known and popular H_2 detector [13,14,17,18,24–31]. In the presence of various Pd nanostructures as nanoparticles (NP) [24,25], hierarchical nanostructure [26], nanowires (NW) or nanotube array (NT) [27,28] and single NW [29,30], the Pd nanoparticles (PdNP) are simple to form and easy to synthesize by a chemical route. However, PdNPs are problematic in terms of isolation and aggregation [24,25]. In addition, PdNPs expand their volume to few percent during H_2 absorption/desorption, which can easily cause non-structural stability in sensors [27–31]. In order to mitigate these problems, single Pd NW has been proposed [30]. However, the complicated fabrication process of single Pd NW is an obstacle for application in practical H_2 sensors. Recently, graphene has been shown to have excellent properties as a potential material to support a PdNP catalyst [13,14,17] or form Pd-graphene (Pd–Gr) nanocomposites [18,31], and has produced attractive results for H_2 sensing in terms of high sensitivity and stability.

Even though PdNP as catalyst decorated on graphene for high performance H_2 sensor with advantages of wafer-scale [9] and flexibility [14] were reported previously. The graphene was synthesized on copper (Cu) foil by CVD [9,14] still yield high cost in final sensor device by complicated process. With respect to applications, graphene-based devices from GO have significant advantages in terms of scale (with low cost process) and reproducibility compared with graphene from mechanical exfoliation or CVD [21,22]. A similar method with our work in this manuscript to prepare Pd–Gr composite for H_2 sensor from GO solution and Pd precursor were also reported in [18,31]. However, the layer-by-layer deposition [18] of Pd NPs on graphene showed weak bonding between Pd–Gr, leading to less cross-selectivity toward H_2 gas and was significant influenced from testing environment (wet or dry air) on H_2 sensing performance. The fast response and recovery H_2 sensor using single aggregation of Pt–Pd–Gr of size 10 μm between gold interdigitated electrodes [31] raised some problems in experimental reproducibility and batch fabrication process. In this work, we synthesized and investigated a Pd–Gr composite for resistivity H_2 sensors and evaluated the influence of PdNP size in Pd–Gr composite on sensor performance. The sensors were fabricated in terms of large scale and batch process.

2. Experimental

Graphene oxide (GO) was prepared from extra pure graphite powder (Merch, 99.99%) according to Hummers method [32]. Pd–Gr nanocomposites were synthesized by a simple, one step process using 25 ml of a GO aqueous solution (with fixed concentration of 1 mg/ml) and 25 ml of DI water containing varying concentrations of palladium chloride ($PdCl_2$, Aldrich, 99%). The $PdCl_2$ concentrations were 0.05, 0.25, and 0.5 mg/ml for the Pd–Gr-1, -2, and -3 nanocomposite samples, respectively. At first, 25 ml of the GO solution was mixed with 25 ml $PdCl_2$ with rigorous stirring for 2 h at room temperature to complete ion exchange between GO and the palladium ion precursor. Next, 500 μL hydrazine monohydrate ($N_2H_4.H_2O$, Aldrich, 65 wt.%) as a reduction agent was added to mixture (GO + $PdCl_2$) with additional stirring for 6 h at an elevated temperature of 100 °C. The resulting 50 ml stable suspension, which was black, was used to fabricate resistivity sensors. In brief, Pd–Gr composites were deposited on a SiO_2/Si substrate by air-brush spraying (Hansa 381, N_2 as carrier gas) from 2 ml above the suspension. The SiO_2/Si substrate as a sensor chip was divided into several pieces with a fixed size of 0.5×1 cm^2. Before spraying Pd–Gr on SiO_2/Si, the substrate was cleaned with an ultrasonic bath of DI water and acetone. The SiO_2/Si substrate was heated on a hot-plate at 200 °C during spraying. Two Ohmic contacts were fabricated with gold (Au) deposition on the surface of Pd–Gr/SiO_2/Si via a metal mask using RF sputtering (150 W, 7 mTorr working pressure); the diameter of the contacts was 1 mm and the distance between the two contacts was 0.9 cm. A one step post-annealing process was applied to improve PdNP quality and Pd–graphene bonding for H_2 sensing in all samples was carried out by Nextron RTP-1200 in Ar gas environment in 30 min at 400 °C.

The crystalline characteristics of the Pd–Gr nanocomposites were investigated using X-ray diffraction (XRD) with CuKα radiation (1.5406Å) by XPERT-PRO. The surfaces of Pd–Gr nanocomposites were characterized using a JSM-6500F field emission scanning electron microscope (FE-SEM). The at.% (atomic percent) of Pd decorated onto graphene flakes