Sensors and Actuators B xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

E-textile gas sensors composed of molybdenum disulfide and reduced graphene oxide for high response and reliability

Yong Ju Yun[a], Won G. Hong[b], Do Yeob Kim[c], Hae Jin Kim[b], Yongseok Jun[a], Hyung-Kun Lee[c,d,*]

[a] Department of Materials Chemistry and Engineering, Konkuk University, Seoul, Republic of Korea
[b] Division of Electron Microscopy Research Group, Korea Basic Science Institute, Daejeon, Republic of Korea
[c] ICT Materials & Components Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon, Republic of Korea
[d] Department of Advanced Device Technology, University of Science & Technology, Daejeon, Republic of Korea

ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form 1 December 2016
Accepted 4 December 2016
Available online xxx

Keywords:
Molybdenum disulfide
Reduced graphene oxide
Cotton yarn
NO_2 sensor
Electronic textile

ABSTRACT

Textiles with electronic functions (*e*-textiles) have been investigated due to a raise of internet-of-things (IoTs) and wearable electronics. The authors reported *e*-textile gas sensors based on reduced graphene oxides (RGOs) which were coated on the commercially available yarns treated with Bovine Serum Albumin (BSA) as a molecular glue. The *e*-textiles show sensitive responses to NO_2 (25%@4.5 ppm) and durabilities to washing and bending stresses. This study reports an ultrasensitive response of an *e*-textile to NO_2 using combined sensing materials of transition metal disulfide (TMD) and RGO. The *e*-textile covered with MoS_2 and RGO shows a 28% response to 0.45 ppm of NO_2 gas which is one of the most sensitive responses using RGOs as sensing materials.

1. Introduction

A variety of *e*-textiles have been investigated to find applications such as energy storage/generator systems, actuators, sensors, display devices, *etc.* due to the advantages of textiles including pliability, light weight, and cheap manufacturing cost [1–10]. Reportedly, textile sensors can respond to or measure temperature, humidity, force, and pressure through intrinsic or extrinsic modifications of textiles with various functional materials [6–8]. However, the sensors based on textiles should be washable, non-toxic, and resistant to surface shear and environmental stress.

Two-dimensional (2D) layered materials are ideal candidates for the development of reliable and practical electronic sensors due to their exceptional electrical properties and large specific surface area [11,12]. They also have an outstanding mechanical flexibility and chemical stability – very important characteristics for flexible/wearable electronic devices [13,14]. Furthermore, their planar habit offers relative ease of fabrication and the requisite large scale integration.

Among these 2D materials, graphene and reduced graphene oxide (RGO) have been studied extensively for chemical sensor applications owing to their high electrical conductivity, low signal-to-noise level, and stable response to target analytes [15,16]. Furthermore, these materials can be operated at room temperature, which is impossible for traditional gas sensing materials like metal oxide based semiconductors [16].

More recently, molybdenum disulfide (MoS_2), a representative 2D transition metal dichalcogenides (TMDs), is being explored as a promising chemical sensing material for flexible/wearable gas sensors due to its unique semiconducting characteristics [14,17,18]. In addition, MoS_2 based gas sensors exhibit much higher selectivity than carbon nanotube materials [19].

Here we first report an ultrasensitive, washable, and flexible gas sensor composed of few-layer MoS_2 and RGO-coated cotton yarn (CY_RGO) that exhibits ultrahigh sensitivity of NO_2 at room temperature and high reliability under 100 laundry tests and 1000 bending tests with an extreme bending. CY_RGO gas sensor as both electrode and channel was obtained from GO wrapping through an electrostatic self-assembly using BSA as biological glue and a low-temperature reduction. The MoS_2 sheet as an active material was then coated on the CY_RGO by simple dip-coating of a suspension of a few layers of MoS_2 sheet. By combination of the MoS_2 with RGO, this hybrid sensor exhibited ultrahigh sensitivity, which is about at

* Corresponding author at: ICT Materials & Components Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon, Republic of Korea.
E-mail addresses: hklee@etri.re.kr, hklee75@gmail.com (H.-K. Lee).

http://dx.doi.org/10.1016/j.snb.2016.12.028
0925-4005/

two times higher than that of the CY_RGO gas sensors. Furthermore, the sensors exhibit high reliability under 100 repetitive laundry tests and more than 1000 bending tests with an extreme bending radius of as low as 1 mm. The *e*-textile based gas sensor provides a simple route to an essential sensing component of future wearable electronics.

2. Experimental details

2.1. Materials

Graphite powder (SP-1 graphite) was purchased from Bay Carbon (Michigan, USA). Bovine Serum Albumin (BSA) powder, hydroiodic acid (HI), acetic acid (CH_3CO_2H), copper nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$), sodium bicarbonate ($NaHCO_3$), sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), and potassium permanganate ($KMnO_4$) were purchased from Sigma-Aldrich (Korea). MoS_2 solution was purchased from 2D semiconductors (USA).

2.2. Preparation of MoS_2 flake solution

Colloidal solution of MoS_2 sheets in distilled water at a concentration of 2 mM was prepared with the aid of ultrasonicator. Fig. 1(a) shows a photograph of MoS_2 flakes dispersed solution obtained by chemically-exfoliated process. Most of MoS_2 flakes during atomic force microscopy (AFM) measurements have a thickness of 3.0 nm, as shown in Figs. 1(b) and (c), revealing that the multilayer structure of MoS_2 flakes.

2.3. Fabrication of MoS_2/RGO hybrid yarns (CY_RGO_MoS_2)

Fig. 2 shows a schematic diagram of the MoS_2/RGO hybrid yarns (CY_RGO_MoS_2) fabrication process. RGO yarns were prepared by our previous reports [20,21]. Graphene oxide yarns (CY_GO) are prepared by depositing GO sheets on bovine serum albumin (BSA) coated cotton yarns. GO flakes and BSA molecules are charged in aqueous solutions, which depend on especially the pH value. A uniform coating of GO sheets was formed on the BSA-coated cotton yarn through electrostatic self-assembly. The CY_GOs are chemically reduced at 40 °C by immersing them in a solution of 2.0 ml of HI acid (57 wt% in H_2O) and 5.0 ml of acetic acid (>99.7%). Subsequently, the CY_RGO is rinsed with a saturated sodium bicarbonate ($NaHCO_3$) solution and then with distilled water, and finally dried at room temperature. After chemical reduction, we found that the intensity ratio of the D peak and G peak (I(D)/I(G)) increased from 1.02 to 1.56 indicating that the CY_GO was chemically converted into the CY_RGO. (Fig. S1)

For the CY_RGO_MoS_2, the RGO yarns were cleaned with oxygen plasma (low power level: 6.8 W) for 10 min and then dipped into a 2 mM MoS_2 flake solution for 30 min. Afterwards, the samples were rinsed with deionized (DI) water and gently dried with nitrogen gas.

2.4. Characterization

The thickness and lateral size of the dispersed MoS_2 flakes on silicon substrate were obtained by AFM (Veeco, DI3100) with a shaph silicon probe (radius of curvature of the tip was <5 nm). All samples were analyzed using field emission scanning electron microscopy (FESEM, JEOL-6701F, JEOL Company, USA and FESEM, GeminiSEM 300, Carl Zeiss, Germany). Energy dispersive X-ray spectroscopy (EDX) spectrum of samples was measured with in the range of 0–10 keV using SEM-EDX system (SEM-EDX, JEOL-6701F, JEOL Company, USA and SEM-EDX, GeminiSEM 300, Carl Zeiss, Germany). Raman spectra were measured using a micro-Raman system (LabRAM HR, HORIBA scientific with excitation energy of 2.41 eV, 514 nm).

2.5. Test of CY_RGO_ MoS_2 for durability to mechanical stress and washing treatments

The sample was placed in a computer-controlled, home-made motorzied actuating system for flexible test. One side of the sample was hold by the fixed stage and the other side was hold by movable stage. Durability test was performed up to 1000 bending cycles with scan rate of 1 cm/s. Electrical characteristics were simultaneously measured using a digital multimeter (NI 4065, National Instruments Corporation). The samples were dipped into a commercial washing detergent solution for 5 min with 250 rpm of stirring speed. Then the cleaned sample was washed with DI water for 5 min with 250 rpm of stirring speed followed by drying process at 110 °C for 10 min. Washing test was performed up to 100 times. The resistances of the air-cooled samples were measured to check the electric property changes by washing treatment.

2.6. Measurement of gas sensing properties of CY_RGO_ MoS_2

1.0–2.0 cm long CY_RGO or CY_RGO_ MoS_2 was put into gas measurement chamber. Two kinds of chambers were used for the measurements of gas sensing characteristics of the yarn samples. One was the 300 cc volume cylindrical chamber that has a quartz observation window at the top. This home-made chamber was used for the measurements at the room temperature. The yarn samples were attached to wiring clips that were mounted on the printed circuit board (PCB). The sample PCB was placed between top and bottom parts of the cylindrical chamber. The other chamber was a home-made tube furnace containing several sample loading ports made of gold. The tube furnace chamber was heated up to 100 °C and utilized for the investigation of the thermal characteristics of the yarn samples. Details of the measurements can be found in the previous report [21].

3. Results and discussion

3.1. Morphology, flexibility, and durability of CY_RGO_MoS_2 gas sensor

Representative CY_RGO_MoS_2 gas sensors are presented in Fig. 3(a). After RGO and MoS_2 flake coating, the color of the CY changed from white to black. Fig. 3(b) and (c) shows FESEM image of the CY_RGO_MoS_2 with an average diameter of 700 μm and high resolution FESEM image of a single CY_RGO_MoS_2 microfiber with an average dimeter of 10 μm. After the MoS_2 flakes coating was applied, a single CY_RGO_MoS_2 microfiber (Fig. 3(c)) shows individual MoS_2 flakes on the surface of the CY_RGO compared with a single CY_RGO microfiber (Fig. S2), which could be attributed the successful coating of the MoS_2 flakes onto the CY_RGO.

Raman spectra in Fig. 4(a) and (b) show the characteristic peaks of RGO and MoS_2. Two strong peaks observed at 1357 and 1589 cm^{-1} match well with the D and G bands of RGO, which is agreement with that of RGO coated cotton yarns (Fig. 4(a)) [20]. The two peaks in the lower wave number region associated with hexagonal MoS_2 crystal are at 383 cm^{-1} (in-plane $E_{2g}{}^1$ mode) and 406 cm^{-1} (out-of-plane A_{1g} mode), respectively (Fig. 4(b)) [22]. In addition, energy difference (23 cm^{-1}) between the two Raman peaks confirmed that most of MoS_2 flakes consist of a few layers. The analysis indicates that a few layers of MoS_2 are successfully coated on the CY_RGO. The resulting CY_RGO_MoS_2 was further characterized using EDX. EDX spectrum, shown in Fig. 4(c), exhibited typical MoS_2/RGO composites spectral features such as the C peak (0.277 keV), O peak (0.523 keV), Mo peak (2.293 keV), and

Please cite this article in press as: Y.J. Yun, et al., E-textile gas sensors composed of molybdenum disulfide and reduced graphene oxide for high response and reliability, Sens. Actuators B: Chem. (2016), http://dx.doi.org/10.1016/j.snb.2016.12.028