Polyurethane sponges decorated with reduced graphene oxide and silver nanowires for highly stretchable gas sensors

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ABSTRACT

Unlike the stretchable physical sensors such as stretchable pressure sensors, strain sensors, and temperature sensors, few works have been reported on the stretchable gas sensors. This study presents that stretchable gas sensors can be fabricated by decorating reduced graphene oxide/silver nanowires (rGO/AgNWs) hybrids on the porous polyurethane (PU) sponges using a facile dip-coating method. The sensors show good room-temperature responses to NO_2 gas under both a bending strain (r = 3 mm) and a large tensile strain up to 60%. The response of about -15% is measured at a 50 ppm of NO_2 under a 60% strain. Furthermore, reducing gases like acetone and ethanol can also be detected under the large strains. The results of this study offer a new insight into realization of highly stretchable and easy-to-fabricate gas sensors.

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1. Introduction

Recently, many successful wearable devices with mechanical deformability and desired electrical property have attracted considerable attention due to their promising applications in wide areas such as human-activity monitoring [1,2], personal healthcare [3–5], and artificial skins [6,7]. Gas sensors that detect specific toxic gases play an important role in monitoring environment and securing human being's safety. For instance, they can keenly monitor dangerous gases and vapors produced by industries or vehicles [8,9]. To cope with ever-increasing exposure to hazardous gases, the distributions of which are localized in nature, a need for stretchable gas sensors that can be patched on the skin or fabric is also growing. However, the conventional gas sensors are rigid and unable to survive under strain, which severely limits their wearable applications [10–12].

For the past decade, many stretchable physical devices have been developed, including stretchable electrodes, strain sensors, pressure sensors, and transistors [13–21]. However, there have been almost no reports on stretchable devices that have a capability to detect chemical gases. The only report was about gas sensors made of ZnO microtectonic structures, which could detect NO_2 and H_2 gases under a 5% of strain [22]. The ideal stretchable gas sensors should be flexible, extendable, non-toxic, and able to work at room temperature [23]. For the realization of those gas sensors, an important consideration should be paid to the choice of an active material that needs to respond to target gases at room temperature. The conventional gas sensors based on metal oxide semiconductors generally require high working temperatures (200–500 °C) [24–28]. In this regard, reduced graphene oxide (rGO) has a strength, which can detect various gases with high sensitivities at room temperature [29–31]. Furthermore, the rGO can be combined with metal nanoparticles or polymer matrices to produce novel hybrid materials, which exhibit the intriguing properties arisen from the synergistic effects of their individual components [32–35]. Silver nanowires (AgNWs) are one of the most common metal nanomaterials with excellent conductivity. Accordingly, hybrid structures of rGO and AgNWs would be a promising combination as the active gas-sensing material to achieve a room-temperature working gas sensor with moderate resistance. The choice of an elastomeric material that allows the mechanical stretchability is also crucial for implementing the stretchable gas sensors. Employing bulk elastomers such as polyurethane (PU) and polydimethylsiloxane (PDMS) may be difficult due to poor dispersion and limited gas exposure of active materials in bulk elastomer/active material composites. PU sponges, which have shown good deformability in stretchable conductors and strain sensors [36,37], could be an alternative. Herein, the active sensing materials of rGO/AgNWs were elaborately combined with PU sponges to realize the stretchable gas sensors working at room temperature.

In this work, the stretchable gas sensors were fabricated by decorating the rGO/AgNWs hybrids onto the porous elastomeric PU sponges, using a facile dip-coating method. The electrical resistance of the rGO/AgNWs/PU composite sensor could be easily tuned by changing the number of dip-coating cycles. The sensors responded well to NO$_2$ gas under tensile strains of 0, 30%, 40%, and 60%, and even under a bending strain. Moreover, the sensor also responded to reducing gases, ethanol and acetone, under 30% and 60% strains. To the best of our knowledge, this is the first ever report on stretchable gas sensors that show stable responses to both oxidizing gas and reducing gas under a large strain of up to 60%.

2. Experimental

2.1. Materials

Ethylene glycol [C$_2$H$_6$O$_2$, EG], silver nitrate [AgNO$_3$], polyvinylpyrrolidone [PVP, Mw ~40,000], copper (II) chloride dihydrate [CuCl$_2$·2H$_2$O], potassium permanganate [KMnO$_4$], and hydrazine monohydrate [N$_2$H$_4$] were all purchased from Sigma-Aldrich. Sulfuric acid 98% [H$_2$SO$_4$], phosphoric acid 85% [H$_3$PO$_4$], hydrogen peroxide 30% [H$_2$O$_2$], hydrochloric acid 20% [HCl], acetone [(CH$_3$)$_2$CO], and ethyl alcohol [C$_2$H$_5$OH] were purchased from Daejung Chem. Graphite powders were purchased from Bay Carbon (SP-1).

2.2. Synthesis of silver nanowires (AgNWs)

The synthesis process of AgNWs was modified from the previous report [38]. At first, 50 ml of EG was added into a glass flask and preheated to 151.5 °C for 1 h under continuous magnetic stirring. At the preheating step, three reactant solutions of CuCl$_2$, PVP, and AgNO$_3$ were prepared in EG solvent. In particular, the AgNO$_3$ solution was sonicated for 7 min. Then, 0.4 ml of 4 mM CuCl$_2$ solution was added to EG. In 15 min, 15 ml of 0.176 M PVP solution was injected and 15 ml of 0.95 M AgNO$_3$ was added into the flask over the injection time of 30 min. Finally, the colorless and transparent solution changed to bright opaque gray. Then, the mixture solution was cooled down for 24 h in a water bath at room temperature under constant stirring. The reaction mixture was washed three times by centrifugation using acetone. The AgNWs were collected by drying the precipitate in an oven at 70 °C.

2.3. Preparation of reduced graphene oxide (rGO)

Graphene oxide (GO) was prepared by the improved Hummer's method [39]. A 3.0 g of graphite flakes were added to 400 ml of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (360:40 ml) under stirring. Next, a 18.0 g of KMnO$_4$ powder was slowly added to this suspension. Due to the exothermic nature of this process, the temperature of the reaction mixture increased to 35–40 °C. Then, the reaction system was kept and stirred for 12 h in a 50 °C oil bath. At the next step, it was cooled down to 0–5 °C using ice. At the same time, 30% H$_2$O$_2$ was carefully added until the color of the reaction mixture changed to bright yellow. The mixture was centrifuged (4000 rpm) and washed three times with water, three times with 20% HCl. The remaining material was washed with ethanol repeatedly until the pH was close to the neutral point. Finally, the gel-like precipitate was dried overnight in vacuum oven at room temperature. Reduced graphene oxide (rGO) was obtained by reducing GO with hydrazine [40]. A 250 mg of GO was first dissolved in 50 ml DI-water and sonicated for 1 h. 0.25 ml of hydrazine was added to the graphene oxide dispersion and shaked gently by hand. This reaction proceeded for 2 h in a 95 °C oil bath with stirring at 150 rpm.

2.4. Fabrication of rGO/AgNWs/PU composite sensors

At first, rGO/AgNWs solutions with three different weight ratios of rGO to AgNWs were prepared by adding 0.05 g, 0.1 g, and 0.2 g of AgNWs, respectively, into 10 ml of rGO solution and sonicating them for 30 min: they were named rGO/AgNWs-1, rGO/AgNWs-2, and rGO/AgNWs-3, respectively. Sponge pieces (~2.0 × 1.0 × 0.2 cm) were obtained from the commercially available PU sponge. They were cleaned with DI water and ethanol several times, followed by complete drying for 2 h at 70 °C. Then, three pre-cleaned sponge pieces were immersed in rGO/AgNWs-1, rGO/AgNWs-2, and rGO/AgNWs-3, respectively. Finally, they were dried for 1 h at 70 °C. The finally obtained composite samples are named rGO/AgNWs/PU-1, rGO/AgNWs/PU-2, and rGO/AgNWs/PU-3, respectively.

2.5. Material characterization and gas-sensing test

The morphologies of rGO/AgNWs/PU stretchable composites were analyzed by a field emission scanning electron microscope (FE-SEM, JEOL JSM-7500F). To confirm that GO was fully reduced to rGO, X-ray photoelectron spectroscopy (XPS) and UV–vis spectroscopy were utilized. For the respective analyses, a K-alpha spectrometer (Thermal Scientific) with monochromatic Cu Kα radiation ($h\nu$ = 8040 eV) and a UV–vis spectrophotometer (Shimazu UV-2550) were used. A custom-made measurement system (SRVC-1511-LV-4M-D) was used to evaluate the gas-sensing performance of the rGO/AgNWs/PU composites. For that, a composite piece was first put on a SiO$_2$-coated Si substrate and loaded into a gas chamber with a capacity of 200 cc. Then, two contacts were made on both ends of the composite piece using silver paste and the contacts were gold-wired to lead pins of the measurement stage. The gas chamber is connected with multiple gas sources and a gas mixing system, all of which are equipped with individual mass flow controllers (MFC, Tylan 2900), as illustrated in Fig. S2. Target gases such as NO$_2$, ethanol, and acetone were diluted to desired concentrations, using a carrier gas, N$_2$. Target gases with controlled concentrations were fed into the chamber at the same rate of 500 sccm. Electrical testing was remote-controlled and all measured resistances were recorded into a computer by a data acquisition system (Agilent 34970A). In this work, all the tests were performed at a fixed temperature of 30 °C. The response of a composite sensor was defined as the following equation:

$$\text{Response}(\%) = \Delta R/R_{N2} \times 100 = ((R_{gas} - R_{N2})/R_{N2}) \times 100 \qquad (1)$$

where, R_{N2} and R_{gas} are the electrical resistances of the sensor in N$_2$ and the tested gas, respectively.

3. Results and discussion

3.1. Fabrication of stretchable rGO/AgNWs/PU composites

The fabrication method of rGO/AgNWs/PU composite sponges is schematically illustrated in Fig. 1a. AgNWs and rGO were first synthesized by the previously reported polyol and improved Hummer's methods, respectively (see Experimental section for more details) [38]. Next, three types of rGO/AgNWs hybrid solutions were prepared by mixing the rGO dispersion with AgNWs in different weight ratios of 1:1, 1:2, and 1:4 under sonication. Then, pre-cleaned PU sponges with a thickness of 1 mm and an area of 1 × 2 cm^2 were carefully dipped into the rGO/AgNWs solutions. In 3–5 min, the sponges were taken out of the solutions, and finally dried for 1 h at 70 °C. The left picture in Fig. 1b is the SEM image of a pure commercially available PU sponge, which clearly shows three-dimensionally networked structure with most volume composed of micropores [41]. The pore size is in the range of 100–500 μm. The