Sensors and Actuators B 197 (2014) 66–72

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Humidity-sensing properties of chemically reduced graphene oxide/polymer nanocomposite film sensor based on layer-by-layer nano self-assembly

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ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form 19 February 2014
Accepted 21 February 2014
Available online 2 March 2014

Keywords:
Graphene oxide
Layer-by-layer
Self-assembly
Flexible device
Humidity sensor

ABSTRACT

Chemically reduced graphene oxide (RGO)/poly(diallylimethyammonium chloride) (PDDA) nanocomposite film sensor with high-performance humidity properties was reported in this paper. The film sensor was fabricated on flexible polyimide substrate with interdigital microelectrodes structure. By the layer-by-layer nano self-assembly approach, graphene oxide and PDDA were exploited to form hierarchical nanostructure, and then was partially reduced via solution-based chemically reduction for obtaining both conductivity and chemically active defect sites. The effect of hydrobromic acid treatment on the conductivity properties of PDDA/GO film was examined, further verifying the advantage of hydrobromic acid reduction. The humidity sensing properties of the presented nanocomposite film sensor, such as repeatability, hysteresis, stability, response–recovery characteristics, were investigated by exposing to the wide relative humidity range of 11–97% at room temperature. As a result, the sensor exhibited not only excellent sensing behavior to humidity, but also fast response–recovery time and good repeatability, highlighting the unique advantages of layer-by-layer nano self-assembly for film sensors fabrication. As last, the possible humidity sensing mechanism of the proposed sensor was discussed in detail.

1. Introduction

Portable, reliable and low-cost humidity sensors play an important role in many measurement and control applications, including industry, agriculture and environmental fields [1,2]. So far, many efforts have been made to develop high-performance humidity sensors using various transduction techniques, such as capacitance [3], resistance [4], optical fiber [5], field effect transistor (FET) [6], surface acoustic wave (SAW) [7] and quartz crystal microbalance (QCM) [8]. Furthermore, several kinds of sensing materials have been employed in humidity sensors, such as polymers [9], metal oxide [6], carbon nanotubes [3] and composites [4,7], but they have their own advantages and specific conditions of application. Recently, graphene has aroused tremendous interest for various sensing applications mainly due to its large specific surface area for molecular adsorption and outstanding electrical properties such as low noise level and high carrier mobility [10–12]. The application of graphene-based electronic sensors is still in its infancy until now, but their promising performances are remarkable [13–16]. For instance, mechanically exfoliated graphene has demonstrated an effective detection of gaseous species down to the single molecular level [17].

Graphene can be obtained through various physical and chemical routes. Micromechanical cleavage of graphite was the initial approach to produce single-layer graphene, but is not suitable for large-scale production due to its inefficient process and no control over the number of layers [17]. Epitaxial grown of graphene and chemical vapor deposition (CVD) had been reported to fabricate large-area graphene film, however, the two methods are limited for specific conditions of application, such as high temperature, ultrahigh vacuum, and capital equipment dependence [14,18]. An alternative approach to cost-effectively large-scale produce graphene-based devices is to first produce graphene oxide (GO) and then reduce it to obtain graphene for device applications. The basal planes and edges of GO are decorated with many oxygen functional groups, such hydroxyl, epoxy and carboxylic acid groups, which make GO facilitate to form film by solution-based fabrication process [19]. Nevertheless, chemical groups make GO electrically insulating, which enables the inconvenient incorporation of graphene oxide into resistive sensors. Recently, chemically reduction in GO and convert it into conductive state has been reported [20,21].

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http://dx.doi.org/10.1016/j.snb.2014.02.078
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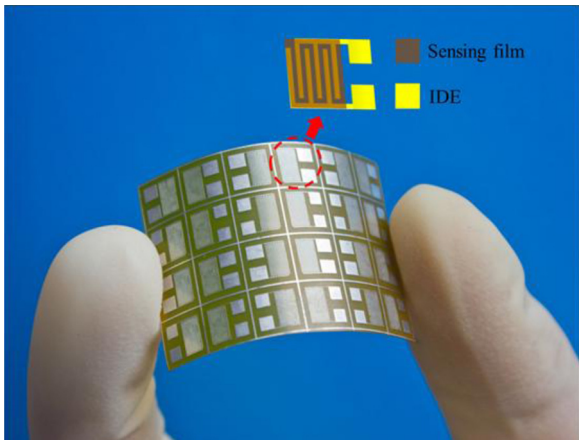

Fig. 1. Optical image of 4 × 6 sensors array on a flexible PI substrate.

In this present work, we fabricated a resistive-type humidity sensor with chemically reduced graphene oxide/poly(diallylimethyammonium chloride) (PDDA) nanocomposite film by using layer-by-layer (LbL) nano self-assembly method. The film sensor was fabricated on flexible polyimide substrate with interdigital microelectrodes structure. The sensing film was characterized by using SEM and XRD. The humidity sensing properties of the presented film sensor were investigated by exposing to various relative humidity environments. As a result, the sensor exhibited excellent sensing properties to humidity at room temperature, demonstrating the unique advantages of LbL nano self-assembly for film sensors fabrication. The possible humidity sensing mechanism of the sensors was also discussed.

2. Experiment

2.1. Materials

The commercially available high-purity graphene oxide (GO) nanosheets (>99%) supplied by Chengdu Organic Chemicals Co. Ltd (Chengdu, China) with thickness of 0.55–1.2 nm and diameter of 0.5–3 μm were employed in our experiment. The GO used was a graphene nanosheet negatively decorated with oxygen functional groups and carboxylic groups located at the sheet surface, facilitating the uniformly dispersion of GO into deionized (DI) water. The GO suspension was 0.25 wt.% in concentration at pH 4.5. Polyelectrolytes used for LbL assembly were 1.5 wt.% poly(diallylimethyammonium chloride) [PDDA (Sigma–Aldrich Inc.), molecular weight (MW) of 200–350 K, polycation] at pH 7.5 and 0.3 wt.% poly(sodium 4-styrenesulfonate) [PSS (Sigma–Aldrich Inc.), MW of 70 K, polyanion] at pH 6.5 with 5 M NaCl in both for better surface coverage. The 40 vol.% hydrobromic (HBr) acid was purchased from Sigma–Aldrich Inc., and used as received.

2.2. Fabrication

The humidity sensor was fabricated on a flexible polyimide (PI) substrate through microfabrication technology, including spin coating of photoresist, exposure, development, and lift-off technique. Ni/Cu interdigital electrode (IDE, 20 μm thick) was sputter-deposited on the PI substrate (75 μm thick). The IDE pattern window on the PI substrate provided an outline dimension of 5 mm × 5 mm, the IDE finger thickness was 20 μm, and the width and gap both was 75 μm. Fig. 1 shows the optical image of 4 × 6 sensors array on the PI substrate, a good flexibility for the sensor is observed. Fig. 2 illustrates the layer-by-layer (LbL) self-assembly process of graphene oxide film as sensing materials. First, two

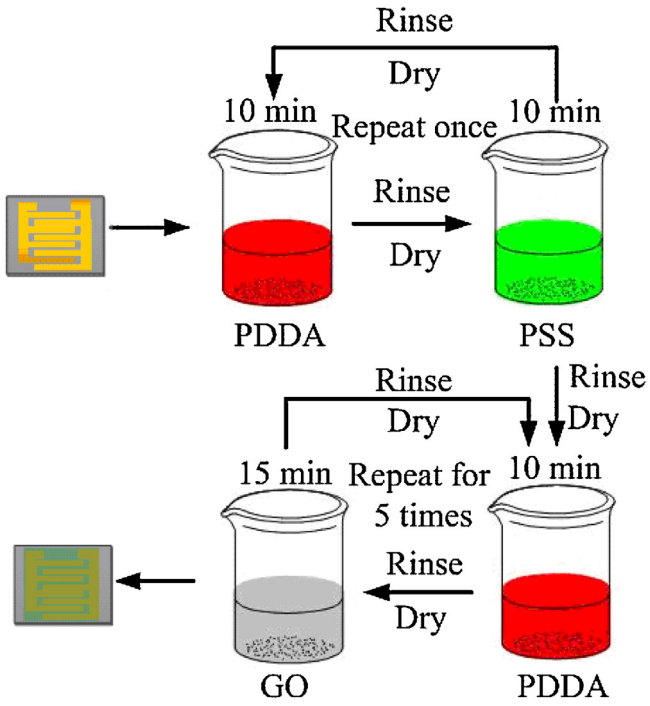

Fig. 2. Layer-by-layer fabrication process of PDDA/GO nanocomposite film.

bi-layers of PDDA/PSS were self-assembled as precursor layers for charge enhancement, followed by the alternative sequence of the immersion into PDDA and GO suspensions for five repetitive cycles. The immersing time here used was 10 min for polyelectrolytes and 15 min for GO, and intermediate rinsing with DI water and drying with N_2 were required after each monolayer assembly to reinforce the interconnection between layers. Finally, the device was placed in the oven at 50 °C for 5–8 h. Thus, five bi-layer PDDA/GO film was performed by using LbL self-assembly technology. Fig. 3 depicts the schematic diagram of the LbL-assembled sensor along with hierarchical structure of sensing films. Subsequently, a simple but highly effective hydrohalic acid reducing method was developed to reduce PDDA/GO films into highly conductive films while maintaining their good integrity. The reduction was carried out by immersing the nanocomposite film devices into HBr acid solution

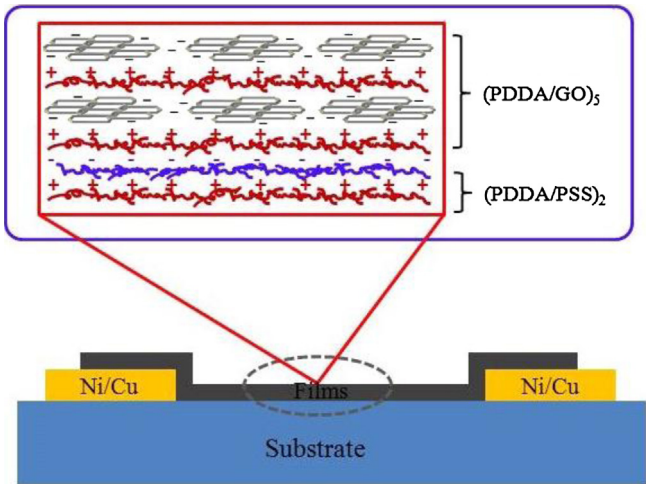

Fig. 3. Schematic diagram of the LbL-assembled sensor along with hierarchical structure of sensing films.