PEDOT:PSS modified Screen Printed Graphene-Carbon Ink based Flexible Humidity Sensor

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***Abstract*—In this work, we present a screen-printed humidity sensor fabricated on a flexible polyvinyl chloride (PVC) substrate. A comparative analysis has been carried out for printed graphene-carbon electrode with and without Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) modification in the humidity sensing range of 25 - 90 %RH. The sensor modified with PEDOT:PSS demonstrated enhanced performance (~ 1 %/%RH versus ~ 0.8 %/%RH of unmodified sensor). Further, the enhancement in the performance of the modified sensor was found to be prominent in the low to moderate humidity range (≤60 %RH). The repeatability, response and recovery time were also analysed for both types of sensors and their applicability has been demonstrated for neonatal care by monitoring the humidity level of a wet baby diapers. This demonstration shows the potential application of presented humidity sensors in areas such as environmental monitoring, healthcare, industrial, and agriculture.**

Keywords—Humidity sensor; PEDOT:PSS; graphene-carbon; flexible sensor; printed electronics

I. Introduction

Humidity is a vital parameter that is needed to assess the environmental, industrial, and medical conditions [1]. Humidity level between 30 - 60 % is considered ideal for human comfort and any deviation could adversely impact the health [2, 3]. Similarly, humidity levels may have considerable impact on crop growth and overall farm production [4]. Industrial humidity is equally important for industries such as semiconductors, and food packaging *etc.* [5, 6]. The wider need for humidity measurement calls for cost-effective indoor/outdoor sensors and as a result various types of mechanisms (e.g., capacitive, resistive, thermal *etc.*) and materials have been explored [7-9]. However, complex synthesis of nanomaterials, costly fabrication of electrodes and non-flexible form factors pose challenges for their widespread use [10-14] . As a result, screen-printing based sensors on flexible and disposable substrates has garnered attention recently. The capability to choose the substrate, ink and the flexibility of designing the electrode provides multiple opportunities to improve the performance of printed sensors. The resource efficient printing of sensitive materials could also lower the costs of sensors and improve their commercial viability [15].

Among sensitive materials the carbon and graphite-based inks have been widely explored for development of various physical, chemical and biosensors [16-18]. Likewise, conductive polymers such as PEDOT:PSS have been widely reported for various sensing and optoelectronic applications [7, 19, 20]. Drop casted film of PEDOT:PSS over gold electrodes has been previously reported as a chemiresistor and displayed a saturation of 80% RH [21]. In recent years, several modifications such as the addition of polymers, metal oxides and carbon-based materials have been added to PEDOT:PSS to improve the mechanical stability, and the overall sensitivity over a broad range of humidity sensing [22]. However, the use of metal-based inks for electrode fabrication as well as the complex fabrication route opted to synthesise various sensing materials to improve the sensitivity as well as increase the range of humidity detection, adds to another layer of complication. Therefore, the ease of fabrication of sensors from these materials is still a challenge. Herein, we report a simple strategy for development of humidity sensor involving the drop casting of PEDOT:PSS over a screen-printed graphene-carbon ink based flexible electrodes. The use of biocompatible graphene-carbon ink for printing electrode aids in evading the use of toxic metal-based inks without compromising the conductivity of the printed sensor not at a large extent. The PEDOT:PSS based modified sensor displays a wide range (25 %RH - 90 %RH) of humidity sensing operation. Specifically, the enhancement in the performance of the modified sensor was found to be prominent in the low to moderate humidity range (≤60 %RH). The repeatability, response and recovery time were also analysed for the sensors and their applicability has been demonstrated for neonatal care by monitoring the humidity level of a wet baby diapers. The wettability of the diaper was monitored and displayed efficient sensitivity compared to the unmodified sensor.

This paper is organised as follows: The materials and methods used for the development of sensors are given in Section II. The results from evaluation of humidity sensors are given in Section III and the key outcomes are explained in Section IV.

II. Materials and Methods

A. Materials

PEDOT:PSS was purchased from Ossila PH 1000. The graphene carbon ink for electrodes was purchased from Sun chemicals (C2171023D1: Graphene Carbon Ink:BG04). For insulating the wires, dielectric grey ink from Sun chemicals was used.

B. Fabrication of sensor:

The humidity sensor, shown in Fig. 1, was obtained by screen printing graphene-carbon ink on a flexible PVC substrate, with the help of the screen printer from Aurel Automation (Screen Stencil Printer C920). The freshly printed sensors were annealed at 60 ºC in an oven for 60 minutes. After this the wire connections were made with

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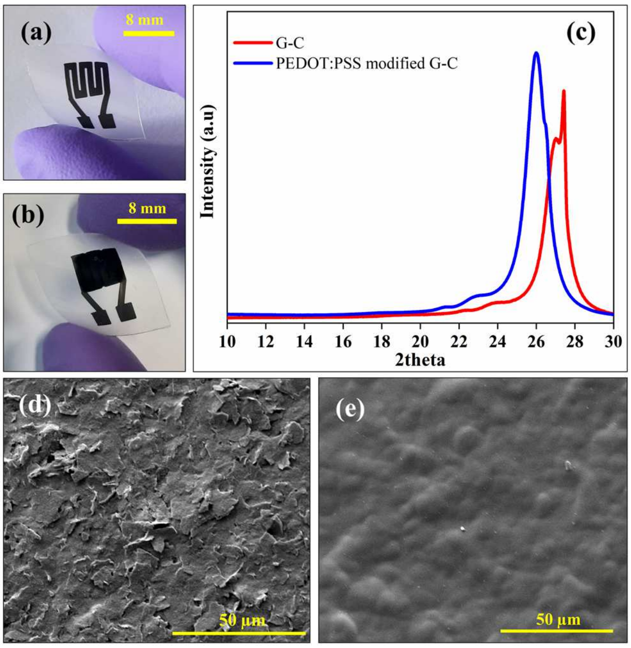

Fig. 1 (a) Screen-printed graphene-carbon (G-C) ink based flexible humidity sensor (sensor1), (b) PEDOT: PSS modified screen-printed graphene-carbon ink-based humidity sensor (sensor2), (c) XRD of sensor1 and sensor2, SEM images of the (d) G-C layer and (e) PEDOT:PSS modified G-C layer at 50 µm scale.

electrodes for 2-wire resistance measurements and the contacts were insulated using the grey dielectric ink and left for curing in the heating oven at 60 ºC for 30 minutes. Here, the unmodified fabricated graphene-carbon sensor was considered as sensor1, shown in Fig. 1(a). For the sensor2 (shown in Fig. 1(b)), further modification was introduced by drop casting 30 µL of PEDOT:PSS over the graphene-carbon printed electrode and left for drying at 40ºC overnight.

C. Humidity sensing setup:

For humidity sensing, an acrylic sensing chamber (50 cm x 40 cm x 45 cm) was built with few holes in the front and side panels. This chamber consists of a humidifier unit and a sensor holder, which were placed inside the chamber. The top panel was closed airtight with a rubber seal. The holes on the sides of panels were used to insert (i) commercial humidity meter tip for calibration, (ii) sensor cable for outlet measurement, and (iii) a power cord for the humidifier unit. Here PureMate (PM 908 Digital Ultrasonic Cool Mist Humidifier) was used as the humidifier unit, which can be used for both generating and regulating humidity condition inside the chamber. For the calibration, commercially available ATP - Humidity & Temperature Meter DT-625 was used as the reference humidity meter (with ±2%RH accuracy). The measurements were carried out using Agilent 34461A 6½ Digit Multimeter and the change in resistance was recorded using the associated LabVIEW interface. For the dehumidification process, the top panel of chamber was set open, and sensor was exposed to ambient air.

III. Results and Discussion

A. Material characterisation

The graphene-carbon ink-based sensor1 is depicted in Fig. 1(a). The PEDOT:PSS modified graphene-carbon ink-based sensor2 is depicted in Fig. 1(b). The flexible nature of the developed sensors makes them suitable for several application areas mentioned earlier. The X-ray diffractograms of the sensor1 and sensor2 is displayed in Fig. 1(c). Sensor1 shows a strong broad peak at ~27º, which is characteristic of carbon for (002) plane [23]. The broadness of the peak is attributed to the presence of graphene nanosheets. The modified sensor (sensor2) also displays a broad peak at ~25º, which is characteristic of PEDOT:PSS for (020) plane, attributed to the π–π stacking of the PEDOT chain [24, 25]. The successful modification of a uniform sensing layer is confirmed by the absence of any peaks attributed to the graphene-carbon ink.

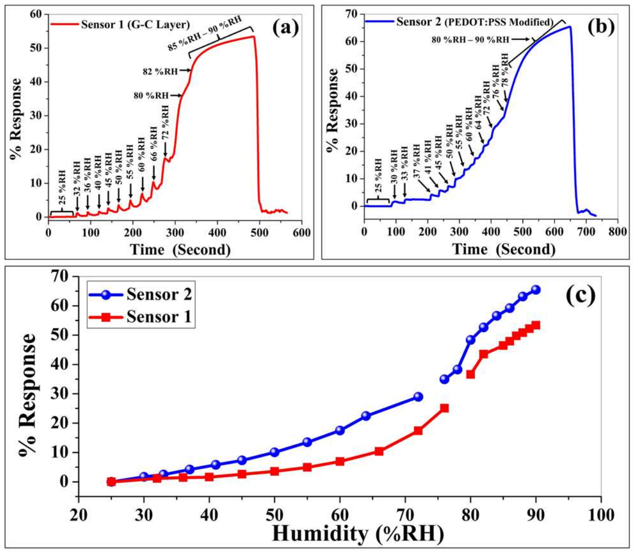

Fig. 2. Humidity sensing characteristics of sensor1 and sensor2 for 25 % RH to 90 % RH range. Dynamic response characteristics of (a) sensor1 and (b) sensor2. (c) % Response analysis for sensor1 and sensor2.

To examine the surface morphology of the sensing layer of both the sensors, scanning electron microscopy (SEM) analysis was carried out. The SEM images of the graphene-carbon layer and PEDOT: PSS modified graphene-carbon layer are shown in Fig. 1(d-e). Randomly distributed graphene-carbon network is observed for sensor1. Post modification with PEDOT: PSS, the changes of sensing layer (sensor2) are observed in surface morphology. Thus, the SEM images confirm the uniform modification of the sensing layer with PEDOT:PSS over the graphene-carbon electrode.

B. Humidity sensing analysis

The dynamic humidity sensing characteristics of sensor1 and sensor2 are displayed in Fig. 2. The humidity sensing response of both the sensors is investigated within 25 to 90 %RH humidity range at room temperature (27 ºC ± 2 ºC). The resistance of both sensors was found to increase with increase in percentage of relative humidity (%RH). The dynamic response characteristics of sensor1 and sensor2 under intermediate humidity levels (within target range) are displayed in Fig. 2(a-b), respectively. The % response used to determine the sensing performance as follows [26]:

$$\frac{\Delta R}{R_A} \times 100 \qquad (1)$$

Where, $\Delta R = R_H - R_A$; R_H and R_A are resistance of the sensor determined at particular humidity level and baseline resistance (analysed at 25 %RH), respectively.

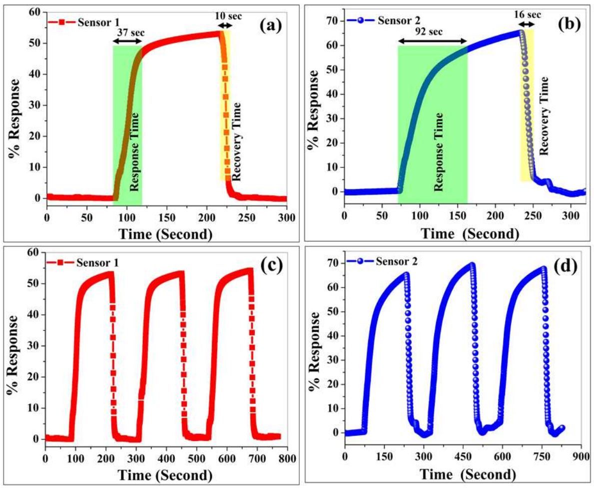

Fig. 3. Response and recovery time analysis for (a) sensor1 and (b) sensor2 within humidity range 25 %RH to 90 %RH. Three-cyclic repeatability analysis for (c) sensor1 and (d) sensor2 within humidity range 25 %RH to 90 %RH.

The comparative analysis of % response for sensor1 and sensor2 is shown in Fig. 2(c). The % response calculated for sensor1 is ~53 % and it is ~66 % for sensor2 at 90 %RH. The PEDOT:PSS modified G-C based sensor2 displayed enhanced humidity sensing performance for the measured range *i.e.*, 25 %RH - 90 %RH, compared to sensor1. Specifically, the performance of sensor2 is comparatively more prominent towards low to moderate humidity range (below and around 60 %RH). In general, PEDOT:PSS exhibits a core shell like structure with PEDOT forming the core and PSS forming the shell. These molecules are sensitive to water molecules, as the humidity level increases, the hydrogen bond between the PSS and PEDOT weakens [27-29]. This results in enhanced distance between the core and the shell molecules, which effectively contributes to increased distance for the electrons to migrate and leads to enhanced resistance with the increase in humidity level [7].

The response and recovery time was also analysed for both sensor1 and sensor2. The time taken by the sensor to reach ~ 90 % of maximum resistance change under humidity and ambient air is used to determine the response and recovery time, respectively [26]. As shown in the Fig. 3(a-b), the response/recovery time is observed as 37s / 10s for sensor1 and 92s / 16s for sensor2. Comparative analysis shows that the sensor2 is sluggish as compared to sensor1. Whilst, modification of the sensor2 results in improved sensitivity towards humidity change, it comes at the cost of response/recovery time. Introduction of PEDOT:PSS layer over the sensing electrode introduces a new pathway for the electron migration. Moreover, the increased resistance with the increase in the humidity level, between the modified layer as explained previously, also contributes towards the delayed response measured. Further, the repeatability analysis was performed for both the sensors. Three cyclic measurements are carried out for sensor1 and sensor2 in humidity range 25 %RH to 90 %RH as shown in the Fig. 3(c-d). The obtained results clearly represent the repeatable behaviour of both the sensors, which makes them suitable for multiple times utilization.

C. *Sensor application*

The suitability of the fabricated flexible sensors was investigated for neonatal care application by monitoring the wettability of baby diapers. The monitoring of wet baby diapers is crucial, as wet diapers or infrequent change of diapers can cause inflamed skin or rashes [30]. Both sensor1 and sensor2 were attached on bottom side of the diaper and tested individually. Experimental set-up for humidity monitoring over a diaper is shown as in Fig. 4(a). Initially, the humidity of the fresh diaper (without water) and wet diaper (with 50 mL water) is monitored using commercial humidity meter and it was found to be ~30 %RH and ~63 %RH, respectively. Further, the response of sensor1 and sensor2 is determined for both the cases *i.e.,* fresh diaper and wet diaper. As shown in Fig. 4(b), the response for the sensor1 is observed as ~1 % and ~7 % and response of the sensor2 is observed as ~1 % and ~24 % for fresh diaper and wet diaper conditions. The elevated response of the PEDOT: PSS modified graphene carbon layer-based sensor2 clearly portrays its better ability towards neonatal care application. The calculated humidity levels for sensor2 were~28 %RH and ~65 %RH for fresh diaper and wet diaper, respectively. The calculated humidity values are observed in accordance with the actual humidity levels (~30 %RH and ~63 %RH) with an accuracy of ±2 %RH. Therefore, the observed results evidence the suitability of the fabricated sensor2 towards its utilization for neonatal care application.

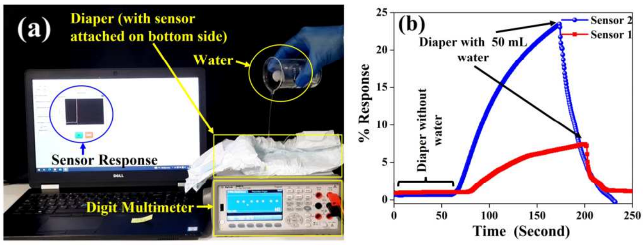

Fig. 4. (a) Experimental set-up for wet diaper's humidity monitoring. (b) Comparative analysis of sensing performance of sensor1 and sensor2 towards wet diaper.

IV. CONCLUSION

In this work, a comparative study has been carried out for a screen-printed graphene-carbon electrode with PEDOT:PSS modification for humidity sensing. The obtained results demonstrate the suitability of the PEDOT:PSS modified graphene-carbon ink based sensor for wide humidity range (25 %RH - 90 %RH). Specifically, the performance of modified sensor is found more prominent towards low to moderate humidity range (≤ 60 %RH) as compared to unmodified sensor. The increased resistance measured with increasing humidity level is attributed to the increased sensitivity of the PEDOT:PSS to water molecules. The adsorption of water molecules results in breaking of hydrogen bonds between the PEDOT and PSS molecules. This results in increased distance for the electron migration and effectively contributing to the increased resistance value. The modification of the sensor1 effectively improves the overall sensitivity of the sensor, especially at lower humidity levels. However, the response is achieved at a small compromise of slower response/recovery time. The modification introduces newer charge migration pathways, and this effectively contributes towards the slower response/recovery time. Finally, the applicability of presented sensor has been demonstrated for neonatal care by monitoring the humidity level of a wet baby diapers. This demonstration also shows the potential application for use of presented humidity sensors in areas such as environmental monitoring, healthcare, industrial, and agriculture

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