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Flexibility and electrical and humidity-sensing properties of diamine-functionalized graphene oxide films

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ABSTRACT

Novel impedance-type humidity sensors were made by coating diamine-functionalized graphene oxide (GO) films on alumina or plastic substrates. Ethylenediamine (EA) and 1,6-hexanediamine (HA) were used to functionalize GO using N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) (EDC/NHS) as the coupling reagent. The effects of the chain length of diamine on the electrical and humidity-sensing properties of the diamine-functionalized GO film were investigated. The diamine-functionalized GO film was characterized by atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The impedance-type humidity sensor that was made of the EA-GO film exhibited a wide range of working humidities, a high sensitivity, satisfactory linearity, a small hysteresis, high flexibility, a short response/recovery time, a weak dependence on temperature and high long-term stability. The linearity of the humidity sensor depended on the applied frequency. The ions (H_3O^+) dominate the conductance of the diamine-functionalized GO film.

1. Introduction

Graphene comprises well separated two-dimensional (2D) layers of aromatic carbon atoms that are covalently linked via sp2 bonds to form a honeycomb sheet [1]. Graphene is critical to many sensing devices because of its high mechanical strength, high surface area, high carrier mobility and high electron transfer at room temperature, and low manufacturing cost [1–3]. Graphene derivatives have many favorable surface properties, which make them useful in various sensing systems [4–6]. The synthetic processes, such as oxidation and surface functionalization, can be regulated to cover the surface of graphene derivatives with large functional groups [4,7]. Obviously, a higher concentration of functional groups corresponds to a greater sensitivity of the sensing system.

The oxidation of graphite using strongly acidic oxidants [8], yields graphene oxide (GO) with hydroxyl and epoxide functional groups on their basal planes, and carboxyl groups at the sheet edges [9]. This GO can be reduced by various reductants such as hydrazine, sodium borohydride and ascorbic acid [10–12]. Recently, many groups have used GO, reduced GO and composite sensing materials to detect humidity [13–18]. Yao et al. [13] fabricated a humidity sensor by spin-coating chemically derived graphene oxide on a quartz crystal microbalance (QCM). Sun et al. [14] fabricated a flexible humidity sensor by spin-coating GO film on PET substrate and then reducing the GO film using two-beam-laser interference (TBLI). Zeng et al. [15] fabricated a humidity sensor by drop-coating defective graphene on alumina substrate. Chen et al. [16] fabricated a stress-type humidity sensor that was based on a graphene oxide-silicon bi-layer flexible structure. Li et al. [17] fabricated a low-humidity sensor by dip-coating composites of poly(diallydimethylammonium chloride) (PDDA)/graphene and poly(4-styrenesulfonate) (PSSNa)/graphene on the surface of the interdigitated gold electrodes. Zhang et al. [18] fabricated a resistive-type humidity sensor with chemically reduced graphene oxide/PDDA nanocomposite film by using layer-by-layer (LbL) nano self-assembly method.

Recently, interest in the surface functionalization of graphene has increased because the functionalization of graphene sheets with appropriates functional groups is required to fabricate various sensors [19,20]. GO has been used extensively as a precursor material in the functionalization of graphene because the graphene sheets in GO are heavily oxygenated. The presence of these chemical groups greatly facilitates the functionalization of graphene sheets by covalent functionalization and non-covalent functionalization [21]. Chemical covalent bonding produces to form stable bonds on the surface of GO. Among various functional groups, the amine group is relatively reactive and can easily react with various chemicals. In many works, the high reactivity of the attached amine groups supports a promising method

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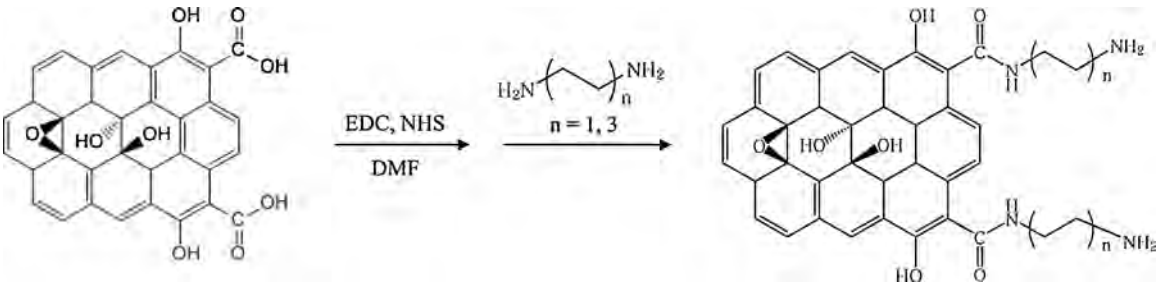

Fig. 1. Schematically illustrates the reaction between GO and diamines.

for fabricating amine-functionalized graphene [22,23] and amine-functionalized graphene/polymer composites [19–21,24,25] and provides a basis for their application. Ryu et al. [23] synthesized amine-functionalized GO films using various alkylamines and studied their surface wettability properties. However, no attempt has been made to fabricate humidity sensors using amine-functionalized graphene materials.

Humidity sensors are widely used in measurement and control of humidity in human comfort and a myriad of industrial processes. Therefore, there has been increasing the important of accurate, precise measurement of humidity. Additionally, designing a high-performance humidity sensor must meet many requirements, including linear response, high sensitivity, fast response time, chemical and physical stability, wide operating range of humidity and low cost. Materials that have been studied for this purpose include polymers and ceramics, which have their own merits and specific conditions of application [26–29]. This work describes the humidity-sensing characteristics of diamine-functionalized GO films that was fabricated by a well-known carbodiimide procedure using N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) (EDC/NHS) as the coupling reagent. Two diamines, ethylenediamine (EA) and 1,6-hexanediamine (HA) were used to react with GO, yielded diamine-functionalized GO films. The electrical characteristics of the diamine-functionalized GO films were studied as functions of RH. The films were characterized by atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The effect of the length of the diamine chain of the diamine-functionalized GO film on its electrical and humidity-sensing properties was studied. The complex impedance spectra were used to explain the role of ions in the conductance of the diamine-functionalized GO film. The flexibility and humidity-sensing characteristics, including sensitivity, hysteresis, response time, recovery time and stability were also investigated, and the effects of applied frequency and ambient temperature were considered.

2. Experimental

2.1. Materials

Graphene oxide (GO; 5 g/L, UniRegion Bio-Tech) was used without further purification. Ethylenediamine (98%; EA), 1,6-hexanediamine (98%; HA) N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (95%; EDC) and N-hydroxysuccinimide (95%; NHS) were obtained from Aldrich. A binding solution, hydrolytic tetraethyl orthosilicate (TEOS) (65%, w/w), was prepared by adding H_2O, C_2H_5OH and some drops HNO_3 (0.25 mL) into TEOS (Aldrich). All reagents used were analytical grade. All used deionized water (DIW) was prepared using a Milli-Q Millipore (Bedford, MA, USA) purification system, and the resistivity of water was above 18.0 MΩ cm^{-1}.

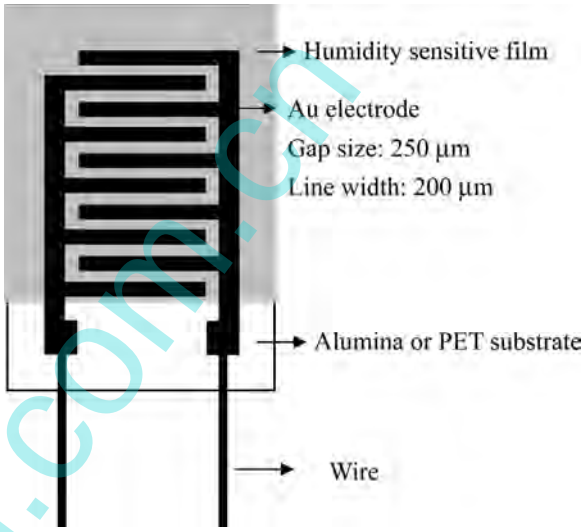

Fig. 2. Structure of humidity sensor.

2.2. Preparation of diamine-GO materials using amidation method

The preparation of diamine-functionalized GO was similar to that used in our previous study by amidation method [30]. Fig. 1 presents the reaction scheme. 1 mL of GO (5 g/L) was sonicated in 20 mL DMF for 1 h, and then 0.2 g of EDC and 0.1 g of NHS were added to the GO solution, which was stirred for 2 h at 0 °C. Finally, 12 mmol of EA was added and stirred at room temperature overnight. The product, EA-GO, was separated by filtration and washed three times with acetone and H_2O to ensure that the excess EA was completely removed. Similar synthetic steps were followed to prepare HA-GO.

2.3. Fabrication of humidity sensors

Fig. 2 schematically depicts the structure of the humidity sensor. The interdigited gold electrodes were made on an alumina substrate by screen-printing method. The interdigited gold electrodes were made on a flexible substrate (polyethylene terephthalate; PET) by sputtering initially Cr (thickness 50 nm) and then Au (thickness 250 nm) in a temperature range of 120–160 °C. The electrode gap was 0.2 mm. The substrates were firstly treated with an H_2O_2/H_2SO_4 mixture (1:2, 15 mL), washed in de-ionized water (DIW) and then cleaned in acetone solution for 3 min. The precursor solution was prepared by adding 3 mg of the as-prepared diamine-functionalized GO and 0.5 mL of the binding solution to 10 mL of DIW, which was then ultrasonically vibrated for about 0.5 h to obtain the well-mixed suspension. Then, the precursor solutions of diamine-functionalized GO were brush-coated onto alumina or

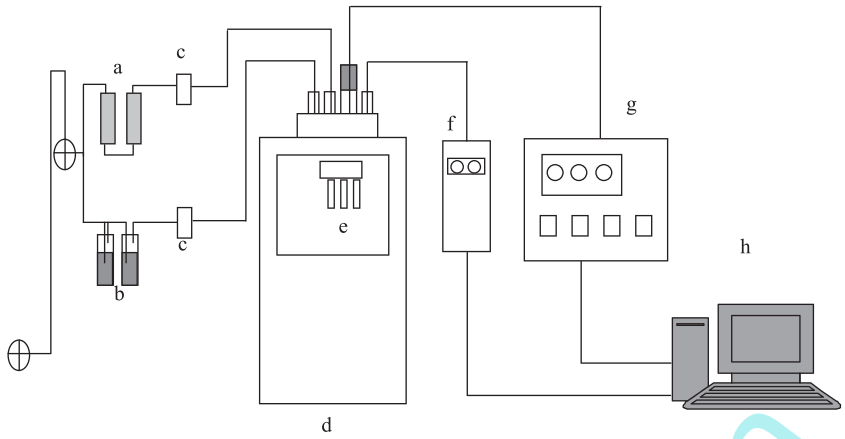

Fig. 3. Schematically plots the impedance measurement of sensors and the humidity atmosphere controller. (a) Molecular sieve and desiccating agent; (b) water; (c) mass flow controller; (d) controlled temperature detection chamber; (e) humidity sensor; (f) hygrometer; (g) LCZ meter; (h) PC.

flexible substrates, which were then thermally treated at 60 °C for 0.5 h in air.

2.4. Instruments and analysis

An infrared spectrometer (Nicolet 380) was used to obtain the IR spectra of the diamine-functionalized GO films. The surface microstructure of the thin film that was coated on an alumina substrate was investigated using an atomic force microscope (AFM, Ben-Yuan, CSPM 4000) in tapping mode which the horizontal and vertical resolution are 0.26 and 0.10 nm, respectively. The impedance of the sensor was measured as a function of RH using an LCR meter (Philips PM6306) in a test chamber under the conditions of a measurement frequency of 1 kHz, an applied voltage of 1 V, an ambient temperature of 25 °C. As shown in Fig. 3, a divided humidity generator was used as the principal facility for producing the testing gases. The required humidity was produced by adjusting the proportion of dry and humid air generated by the divided flow humidity generator under a total flow rate is 10 L/min. The model of two mass flow controller's (Hastings) and flow display power-supply used is the Protec PC-540 manufactured by Sierra Instruments Inc., as described elsewhere [31]. The RH values were measured using a calibrated hygrometer (Rotronic) with an accuracy of ±0.1% RH. Flexibility experiments were performed in which the sensor was bent to various degrees as their responses were monitored as a function of the period of exposure to humidity. The bending angle was measured using a goniometer.

3. Results and discussion

3.1. Preparation and characterization of diamine-functionalized GO films

Fig. 1 shows the reaction procedure of EA- or HA-functionalized GO. EA or HA was covalently bonded to the surface of the GO by forming an amide bond: the carboxylic acid groups in the GO were activated by EDC/NHS (coupling reagent), which reacted with amine groups in the EA of HA to form chemical amide bonds.

3.1.1. Microstructure of surface

The surface morphologies of the GO, EA-GO and HA-GO films were investigated by AFM. Fig. 4 shows the AFM of the GO, EA-GO and HA-GO films on an alumina substrate. The root mean square (RMS) roughness of the GO, EA-GO and HA-GO films was 10.9, 41.6 and 21.6 nm, respectively. The GO film had a smooth surface with flake-like and partially wrinkled structure (Fig. 4(a)). The surface of EA-GO was rougher than that of HA-GO. Additionally, the thickness of EA-GO or HA-GO exceeded that of GO (Fig. 4(b) and (c)), owing to the functionalization of the GO surface by diamine.

Table 1
Sensitivity and linearity of humidity sensors that were made of GO, EA-GO and HA-GO films.

Films	Sensing curve	
	Sensitivity ($\log Z$/% RH)[a]	Linearity (R^2)[b]
GO	−0.0172	0.9794
EA-GO	−0.0545	0.9575
HA-GO	−0.0539	0.9911

[a] Sensitivity was defined as the slope of the logarithmic impedance versus relative humidity plot in the range 20–90% RH.
[b] Linearity was shown as the correlation coefficient of the logarithmic impedance versus relative humidity plot in the range 20–90% RH.

3.1.2. IR spectra

The GO and diamine-functionalized GO films were investigated by IR spectroscopy. Fig. 5 shows the FT-IR results of GO and diamine-functionalized GO, and thereby provides information on the chemical interaction between GO and diamines (EA and HA). The typical peaks of GO appear at 3439, 1658 and 1407 cm^{-1}, corresponding to the O—H stretching vibration, the C=O stretching vibration (COOH group) and the deformation of O—H, respectively. The diamine-functionalized GO exhibited a peak at 1086 cm^{-1}, which is associated with the C—N stretching of the amide group and a peak at 787 cm^{-1} which is associated with the N—H wagging vibration of the amine group. These results confirm that GO was functionalized with diamines.

3.2. Electrical and humidity-sensing properties of humidity sensors made of diamine-functionalized GO films

Fig. 6 plots the impedance of the GO, EA-GO and HA-GO films as functions of relative humidity, and Table 1 summarizes the results concerning sensitivity (defined as the slope of logarithmic impedance ($\log Z$) versus % RH) and linearity (a correlation coefficient that is defined as the R-squared value of the linear fitting curve from 20 to 90% RH). The measurements were made at 25 °C, an AC voltage of 1 V, and a frequency of 1 kHz. When only the binding TEOS solution was used, (as shown in the inset), no change in impedance was observed, revealing that the TEOS negligibly affected the sensing of humidity using GO, EA-GO and HA-GO films. The impedance of the GO film changed by one order of magnitude from 20 to 90% RH, revealing low sensitivity. Functionalization

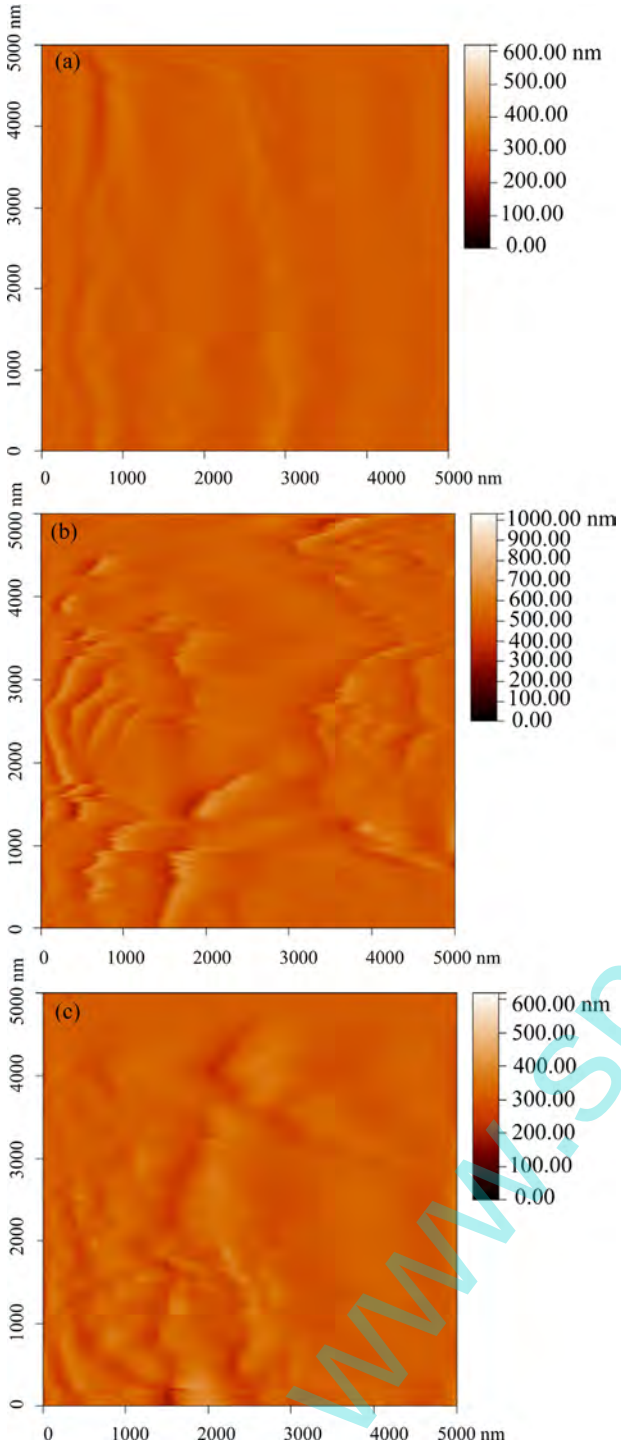

Fig. 4. AFM images of (a) GO; (b) EA-GO and (c) HA-GO films.

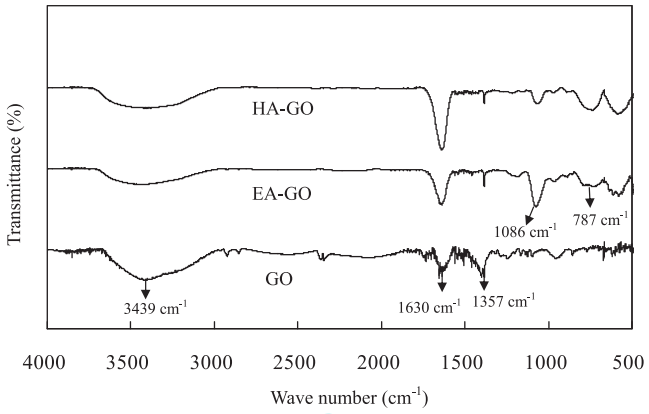

Fig. 5. IR spectra of GO, EA-GO and HA-GO films.

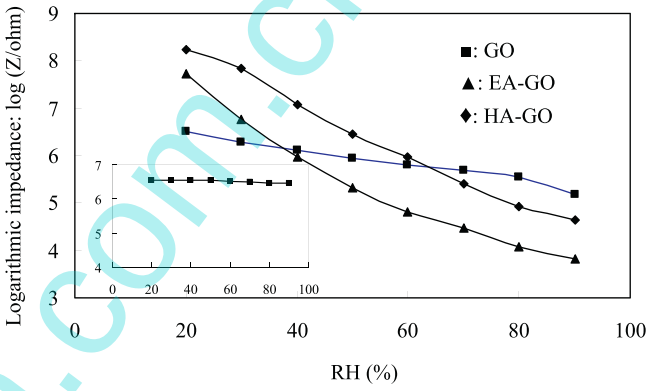

Fig. 6. Impedance versus relative humidity for humidity sensors that were made of GO, EA-GO and HA-GO films coated on alumina substrates. Inset: impedance versus relative humidity for TEOS film.

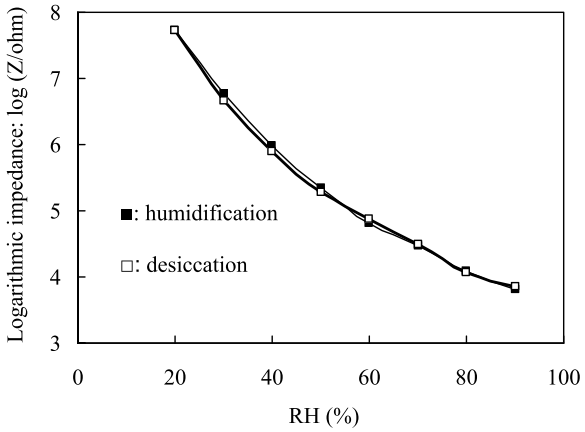

Fig. 7. Impedance versus relative humidity for EA-GO film on an alumina substrate, measured at 1 V, 1 kHz and 25 °C.

of GO films with diamines to form the EA-GO and HA-GO films greatly increased the impedance over a wide range of RH, suggesting that the sensitivity of the response was improved. At low RH (<40% RH), the impedance of the EA-GO and HA-GO exceeded that of GO because the functionalization of graphene with NH_2 groups opened the gap. Moreover, the impedance of the HA-GO was higher than that of EA-GO because the band gap of graphene increased with the length of the alkyl chain of the functionalizing HA [32]. As the humidity increased, the impedance of the EA-GO and HA-GO became increasingly lower than that of GO because the EA-GO and HA-GO films absorbed more water molecules, making more ions (protons (H_3O^+)) available, improving the conductivity. Additionally, the EA-GO film had greater sensitivity than the HA-GO film, because EA has a shorter alkyl chain than does HA, so EA reacts with GO more easily, yielding more sites for adsorbing water molecules, improving the sensitivity of the EA-GO film [22]. Therefore, the flexibility, humidity-sensing properties and sensing mechanism of the humidity sensor that was made of the EA-GO film were studied.

Fig. 7 plots the log-impedance of the humidity sensor versus RH. The measurements were made at 25 °C using an ac voltage of 1 V at 1 kHz. The open symbols in the figure represent measurements made during desiccation, while solid symbols those made

Table 2
Humidity sensor performance of this work compared with the literatures.

Sensor type	Sensing material	Working range	Sensitivity	Hysteresis (% RH)	Response time (s)	References
Impedance-type	Diamine-functionalized GO	20–90% RH	0.0545 log *Z*/% RH	<2	52	This work
Impedance-type	Partially reduced GO	30–90% RH	0.0423 log *Z*/% RH	<2	28	[34]
Impedance-type	Reduced GO	11–95% RH	6.3 *Z*/% RH	<6	~2	[14]
Conductive-type	Defect graphene	3–30% RH	0.27–3.3%	–	–	[15]

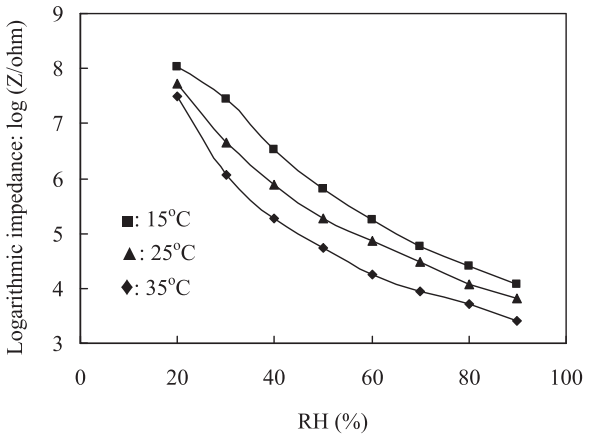

Fig. 8. Impedance versus relative humidity for EA-GO film on an alumina substrate at various temperatures, measured at 1 V and 1 kHz.

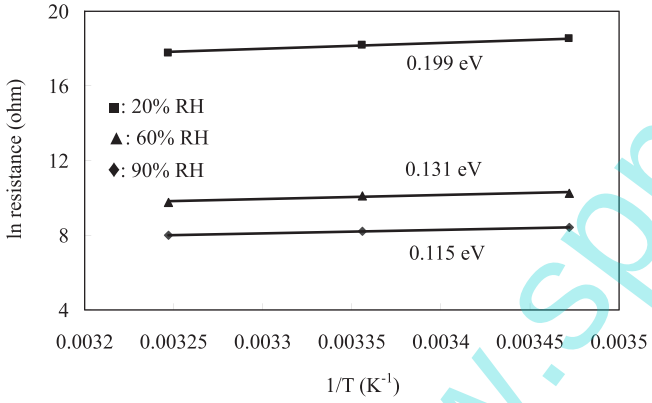

Fig. 9. Resistance versus temperature variation for EA-GO film at 20, 60 and 90% RH.

during humidification. In the range 20–90% RH, the impedance changed from 10^7 to 10^3 Ω and the curves revealed a satisfactorily linear relationship ($Y = -0.0545X + 8.3673$; $R^2 = 0.9575$) between log-impedance and RH. The hysteresis (between humidification and desiccation, measured over an RH range of 20–90% RH) was less than 2.0% RH. Fig. 8 plots the log-impedance of the humidity sensor versus temperature. As the temperature increased, the RH characteristic curve shifted to lower impedance. The mean temperature coefficient at 15–35 °C was −0.40% RH/°C over the humidity range 20–90% RH. When the data were plotted as the measured resistance as a function of $1/T$ at 30, 60 and 90% RH, the activation energy of the sensor was obtained from the Arrehenius plot of resistance, as shown in Fig. 9. The activation energy for conduction is the energy barrier from one stable position to another [33]. The activation energy was decreased from 0.199 to 0.115 eV as RH increased from 20 to 90%. This behavior seems to reflect the fact that ions contribute to the conductivity of EA-GO. Fig. 10 plots the log-impedance of the humidity sensor versus measurement frequency at various RH values at a voltage of 1 V. The frequency clearly influenced the humidity-dependence of the impedance of the humidity

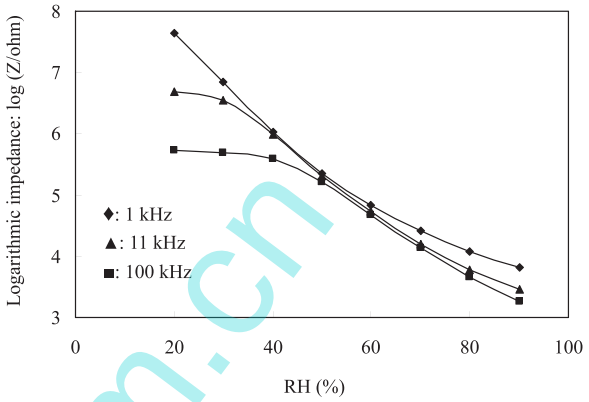

Fig. 10. Impedance versus relative humidity for EA-GO film on an alumina substrate at various frequencies, measured at 1 V and 25 °C.

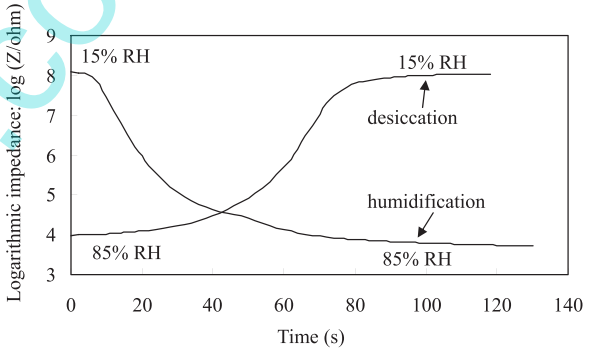

Fig. 11. Response-recovery properties of EA-GO film on an alumina substrate, measured at 1 V, 1 kHz and 25 °C.

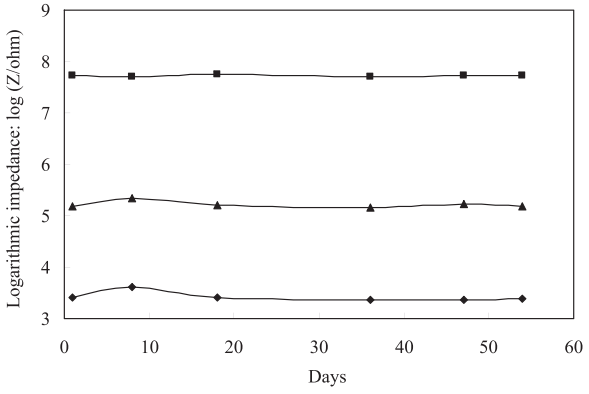

Fig. 12. Long-term stability of EA-GO film on an alumina substrate, measured at 1 V, 1 kHz and 25 °C. (■) 20% RH; (▲) 60% RH; (♦) 90% RH.

sensor. The impedance decreased as the frequency increased, and the curve of impedance as a function of RH was most linear at 1 kHz. Fig. 11 plots the response and recovery of the flexible humidity sensor that was measured at 25 °C and 1 kHz. The response time ($T_{res.95\%}$) is defined as the time required for the impedance of the sensor to change by 95% of the maximum change following

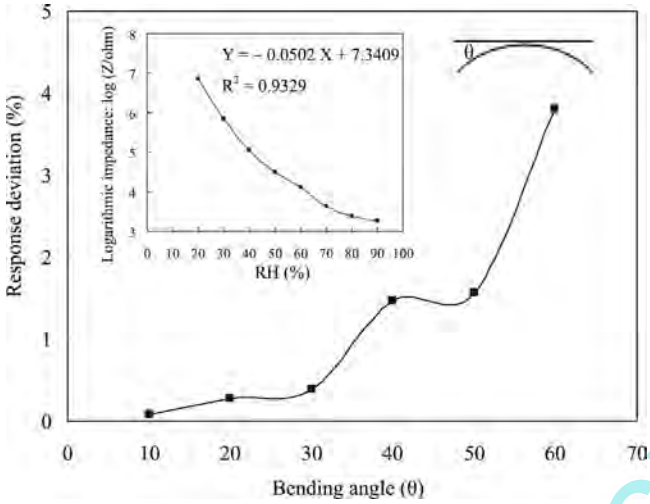

Fig. 13. Flexibility of EA-GO film on PET substrate, measured at 1 V, 1 kHz and 25 °C. Inset: impedance versus relative humidity for the flexible humidity sensor made of EA-GO film.

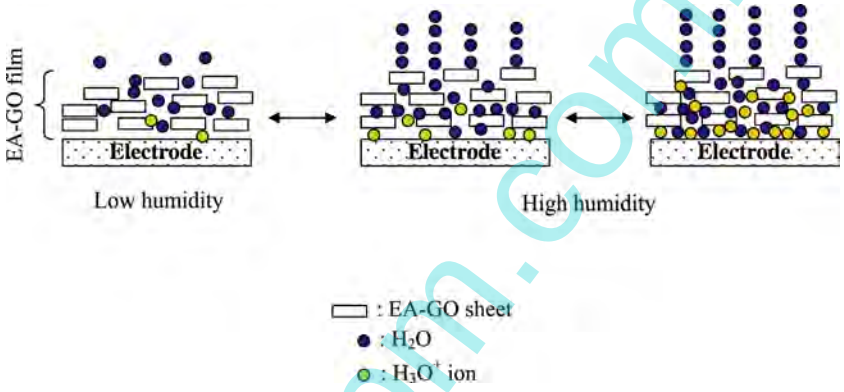

Fig. 14. Schematic drawing to show the humidity response of EA-GO film.

humidification from 15 to 85% RH. The recovery time ($T_{rec.95\%}$) is defined as the time required for the sensor to recover 95% of the maximum change in impedance after desiccation from 85 to 15% RH. The response time ($T_{res.95\%}$) and recovery ($T_{rec.95\%}$) time of the sensor were 52 and 72 s, respectively. Fig. 12 plots the long-term stability. The humidity sensor impedance did not significantly vary for at least 54 days at the tested RH values of 20, 60, and 90% RH. The humidity-sensing properties of the present humidity sensor were compared with those of sensors in the literature [14,15,34] in Table 2.

3.3. Flexibility properties of humidity sensors made of EA-GO film

Fig. 13 plots the flexibility-related characteristics of the EA-GO film that was used as a humidity sensor. The sensor response (S) was calculated according to $S = (\log Z_{30\%\,RH} - \log Z_{60\%\,RH})/\log Z_{30\%\,RH} \times 100\%$, $(\Delta Z/\log Z_{30\%\,RH} \times 100\%)$, where $Z_{30\%\,RH}$ and $Z_{60\%\,RH}$ are the impedance of the flexible humidity sensor at 30 and 60% RH, respectively. At each bending angle, the sensor was exposed to 60% RH. The sensor response deviation (D) was calculated using the formula $D = (S_f - S_b)/S_f \times 100\%)$, where S_f and S_b are the responses of the flat and bent flexible humidity sensor at 60% RH, respectively. When the sensor was bent downward at an angle of up to 60°, the response was changed by <4%. These results reveal that even under an applied stress, the sensor remained highly flexible and it exhibited good electrical performance when it was bent. The log-impedance of the flexible humidity sensor versus RH was shown as the inset. Measurements were made at 25 °C using an ac voltage of 1 V at 1 kHz. The humidity sensing properties (sensitivity and linearity) of the flexible humidity sensor are comparable to those of a sensor that is fabricated on an alumina substrate.

3.4. Sensing mechanism of humidity sensor made of EA-GO film

Fig. 14 shows a model in which ions migrated through the liquid-like solution layer that was formed inside the EA-GO film by the absorption of water, similar to that reported by the authors elsewhere [35,36]. Firstly, upon the adsorption of water, a thin liquid layer formed around the EA-GO sheets or filled the openings in the sensing EA-GO film by capillary condensation or swelling. Second, as the RH was further increased, water molecules were physisorbed in multilayers on the surface of the EA-GO film, forming H_3O^+ ions by dissociation. Finally, at the highest RH (90% RH), the sorbed water acted as a plasticizer, increasing the mobility of the solvated ions (H_3O^+), which dominated the conduction in the sensor.

4. Conclusions

The surface functionalization of GO with amine can enhance its surface properties and increase its sensitivity to humidity. The chain lengths of diamine on GO dominated the electrical and humidity-sensing properties (sensitivity) of the diamine-functionalized GO film herein. The humidity sensor that was made of EA-GO film exhibited good sensitivity and acceptable linearity ($Y = -0.0545X + 8.3673$; $R^2 = 0.9575$) between logarithmic impedance ($\log Z$) and RH in the range 20–90% RH, negligible

hysteresis (within 2.0% RH), a short response time (52 s), a short recovery time (72 s), and good long-term stability (54 days at least), measured at 1 V, 1 kHz and 25 °C. The humidity sensor had high flexibility ($D < 4\%$) when it was bent downward at an angle of up to 60°. The linearity of the humidity sensor depended on the applied frequency. The temperature influence between 15 and 35 °C; found to be −0.40% RH/°C for 20–90% RH. The activation energy was reduced as water was adsorbed. The humidity-sensing by the EA-GO film depended on the ion transport mechanism.

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