



Electrical and humidity-sensing properties of reduced graphene oxide thin film fabricated by layer-by-layer with covalent anchoring on flexible substrate



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ABSTRACT

Novel flexible humidity sensors were fabricated layer-by-layer (LBL) by covalently bonding graphene oxide (GO) to a gold electrode on a plastic substrate using a peptide chemical protocol, and then partially reducing in-situ the GO film. The effects of the duration of reduction of the GO film on the electrical and humidity-sensing properties of the reduced GO film were investigated. The anchored partially reduced GO film was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). This flexible impedance-type humidity sensor exhibited a strong water resistance, a wide range of working humidities, a high sensitivity, an acceptable linearity, a small hysteresis, high flexibility, a short response/recovery time, a weak dependence on temperature and high long-term stability. The flexible humidity sensor's linearity depended on the applied frequency. The complex impedance plots that were obtained at low and high relative humidities revealed that the ions (H_3O^+) dominate the conductance of the anchored partially reduced GO film.

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1. Introduction

Humidity sensors are widely used in measurement and control of humidity in human comfort and a myriad of industrial processes. Flexible sensors has attracted much interest recently because of they have light weight, robustness, low cost and flexible, making them suitable for application in various new areas, such as handheld portable consumer electronics, smart textiles and radio frequency identification (RFID) tags [1–4]. Flexible humidity sensors, fabricated from polymeric materials, have recently been divided into two categories of capacitive-type and impedance-type [5–10]. Oprea et al. developed capacitive-type humidity sensors that were integrated into a flexible RFID tag, based on polycellulose acetate (PCA), polycelluloseacetate-butyrate (PCAB), polymethyl-methacrylate (PMMA) and polyvinylpyrrolidone (PVP) sensing films [5]. Zampetti et al. fabricated a flexible capacitive-type humidity sensor that was made by coating a bis(benzo-cyclobutene) (BCB) film on a polyimide substrate [6]. In our earlier studies [7–9], flexible impedance-type humidity sensors that were made by drop-coating the copolymer of methyl methacrylate (MMA) and [3-(methacrylamino)propyl] trimethyl

ammonium chloride (MAPTAC) (poly-MMA/MAPTAC) [7,8] and TiO_2 nanoparticles-polypyrrole-poly-[3-(methacrylamino)propyl] trimethyl ammonium chloride composite material [9] sensing films on a flexible substrate (polyethylene terephthalate; PET). However one of the serious shortcomings of the hydrophilic humidity-sensing materials is that when exposed to a highly humid atmosphere for a long time, then the humidity sensing layer is liable to swell, shrink or peel off from the substrate [10]. The main challenge for development of flexible sensors is not only their manufacture, but also the stability of their mechanical, electrical and sensing properties under repeated bending.

Graphene comprises a two-dimensional (2D) array of carbon atoms that are covalently linked via sp^2 bonds to form a honeycomb sheet [11]. Graphene has been widely used in batteries, supercapacitors, nanoelectronic and electrochemical sensors because of its high mechanical strength, high surface area, high electron mobility at room temperature and low manufacturing cost [11–13]. Graphene oxide (GO) sheets have recently become attractive as possible intermediates in the manufacture of graphene [14]. In GO, epoxy and hydroxyl groups decorate the surface of carbon sheets and carboxyl groups are localized at the edges [15]. These groups are responsible for the high hydrophilicity and electrical insulation of GO. Besides, by using the chemical or thermal reduction techniques, the GO can be converted to reduced GO, implying that most of the oxygen functional groups in the GO were removed,

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enhancing the electrical conductivity of the reduced GO greatly [16,17]. Therefore, GO and reduced GO have various applications, such as gas sensors [18], and many groups have used GO and reduced GO sensing materials to detect humidity [19–22]. Yao et al. fabricated a humidity sensor by spin-coating chemically derived graphene oxide on a quartz crystal microbalance (QCM) [19]. Sun et al. fabricated a flexible humidity sensor by spin-coating GO film on PET substrate and then reducing GO film using two-beam-laser interference (TBLI) [20]. Zeng et al. fabricated a humidity sensor by drop-coating defective graphene on alumina substrate [21]. Chen et al. fabricated a stress-type humidity sensor that was based on a graphene oxide-silicon bi-layer flexible structure [22]. However, long-term use worsens the performance of these flexible humidity sensors because GO and reduced GO sensing materials are physically coated on the substrates.

Layer-by-layer self-assembly (LBL-SA) method is based on sequential electrostatically adsorptions of ionized polyelectrolytes and oppositely charged materials in aqueous solutions. LBL self-assembly has many advantages over other methods, including simplicity, low-cost, low temperature of deposition, controllable thickness (from nanometers to micrometers) and the need for no complex equipment [23–25]. This approach has recently been adopted to fabricate multi-walled carbon nanotubes (MWCNTs)-glucose oxidase multilayers and SWCNTs on flexible substrates as flexible glucose biosensors [26] and piezoresistive type sensors [27], respectively. In our earlier works [28], a flexible humidity sensor was fabricated by the LBL assembly of poly(2-acrylamido-2-methylpropane sulfonate) (PAMPS) and its salt complex on PET substrates. However, the performance of flexible sensors is worsened by long-term use because the sensing films are not anchored to the substrate. In recent years, since new peptide coupling reagents have been developed for use in organic synthesis, peptide coupling reactions have been widely studied. In a typical peptide coupling reaction, a carboxyl group of a compound is initially activated by a suitable peptide coupling reagent, and it is subsequently reacted with an amine group in another compound [29]. Kwak et al. fabricated a hydrogen peroxide sensor that was made by bonding polyamidoamine (PAMAM) dendrimer onto thiol-modified gold electrodes on a Si wafer using *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) as a peptide coupling reagent [30]. In our earlier work [31], a flexible humidity sensor was fabricated by the LBL anchoring of a copolymer of methyl methacrylate (MMA) and [3-(methacrylamino)propyl] trimethyl ammonium chloride (MAPTAC) film on a 3-mercaptopropionic acid (MPA)-modified Au electrode (MPA/Au) on a PET substrate. However, no attempt has been made to anchor covalently the GO onto a gold electrode on a flexible substrate and then to perform the in-situ reduction of GO to fabricate flexible humidity sensors. In this work, a GO film was covalently anchored onto the cysteamine hydrochloride (CH)-modified gold electrode on a PET substrate using EDC and *N*-hydroxysuccinimide (NHS) (EDC/NHS) as the peptide coupling reagent. This film was reduced in-situ by sodium borohydride (NaBH_4) to form a partially reduced GO film that could be used in a flexible humidity sensor. The films were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The effects of the duration of reduction of the GO film on its electrical and humidity-sensing properties were investigated. The complex impedance spectra were used to explain the role of ions in the conductance of the anchored partially reduced GO film. The water resistance of the anchored partially reduced GO film was investigated. 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.

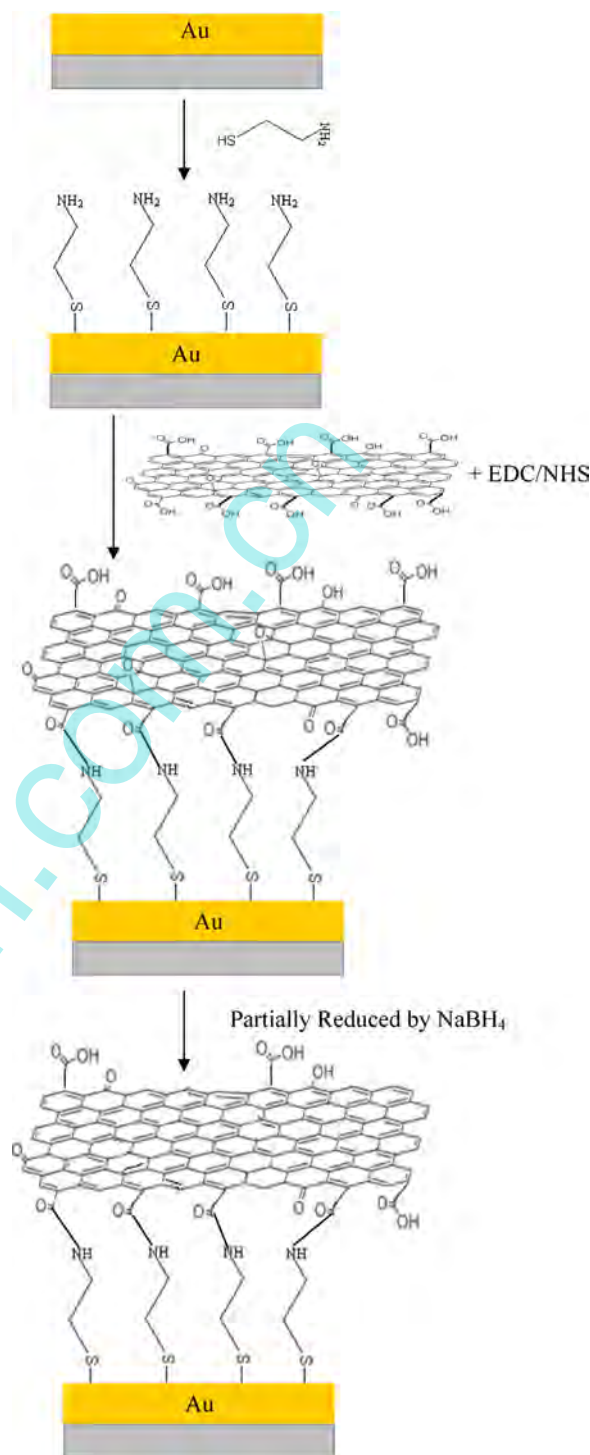


Fig. 1. Fabrication of a flexible humidity sensor by LBL covalent anchoring and in-situ reduction of GO film to reduced GO film.

2. Experimental

2.1. Materials

Graphene oxide (GO; 5 g/L, UniRegion Bio-Tech) were used without further purification. Cysteamine hydrochloride (95%; CH), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (95%; EDC), *N*-hydroxysuccinimide (95%; NHS) and sodium borohydride (95%; NaBH_4) were obtained from Aldrich. All reagents used were analytical grade. All used deionized water (DIW) was

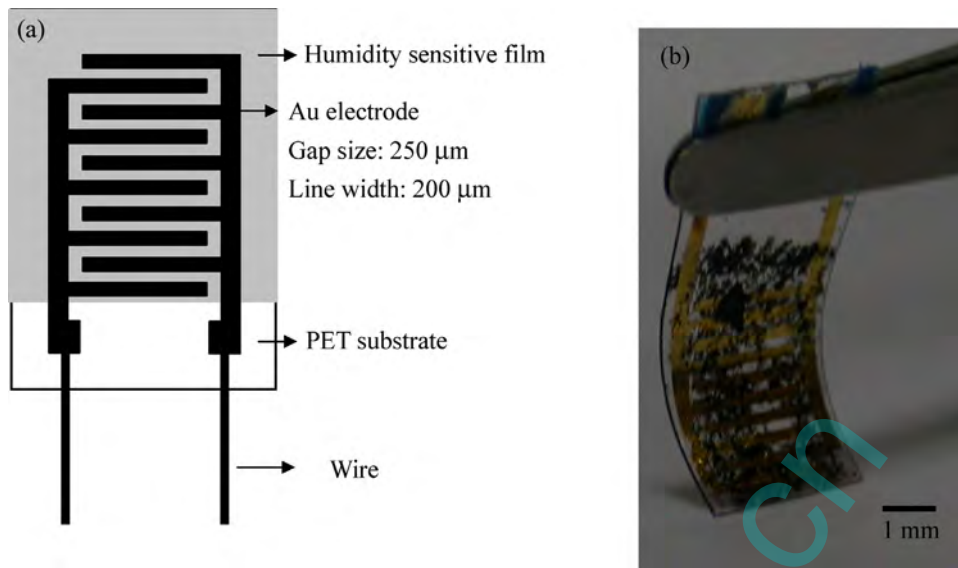


Fig. 2. (a) Structure of flexible humidity sensor; (b) photograph of bent flexible humidity sensor based on reduced GO film anchored on a PET substrate.

prepared using a Milli-Q Millipore (Bedford, MA, USA) purification system, and the resistivity of water was above 18.0 MΩ/cm.

2.2. Fabrication of flexible humidity sensors

The fabrication of a flexible humidity sensor by the LBL covalently anchoring and the in-situ partial reduction of GO on a PET substrate was similar to the method that was used in our previous study [32]. Fig. 1 presents the reaction scheme. Fig. 2(a) schematically depicts the structure of the humidity sensor. The interdigitated gold electrodes were made by sputtering initially Cr (thickness 50 nm) and then Au (thickness 250 nm) in a temperature range of 120 to 160 °C. The electrode gap was 0.2 mm. The substrates were firstly treated with an H₂O₂/H₂SO₄ mixture (1:2, 15 mL), washed in de-ionized water (DIW) and then cleaned in acetone solution for 3 min. The pretreated substrate was immersed in 2.0 mM ethanol solution of CH (75/25% ethanol/DIW) for 24 h at room temperature and then washed thoroughly in 75/25% ethanol/DIW to remove the non-chemisorbed materials. It was then dried at 80 °C to yield a CH-modified electrode (CH/Au). Then, the CH/Au was immersed in 50 μL of GO solution (5 g/L) that contained 200 mM EDC and 400 mM NHS for 12 h at room temperature. It was then

washed thoroughly in DIW to remove any non-anchored GO to form GO-CH/Au. The as-prepared anchored GO film was reduced by immersing the GO-CH/Au substrate in aqueous NaBH₄ (0.04%) for 5 min, rinsing it with DIW and then drying it at 80 °C. Fig. 2(b) shows the flexibility of the reduced GO film that was covalently anchored and reduced in-situ on a PET substrate.

2.3. Instruments and analysis

An infrared spectrometer (Nicolet 380) was used to obtain the IR spectra of the covalently anchored GO and RGO films. The surface microstructure of the thin film that was coated on a PET substrate was investigated using a field emission scanning electron microscope (FEI company, Nova NanoSEM™ 230) and 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 resistance of the sensor was determined as a function of reduction time from the voltage at the ends of the load resistor using a DAQ device (NI, USB-6218) at room temperature of 25 °C and a relative humidity of 40% RH. 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

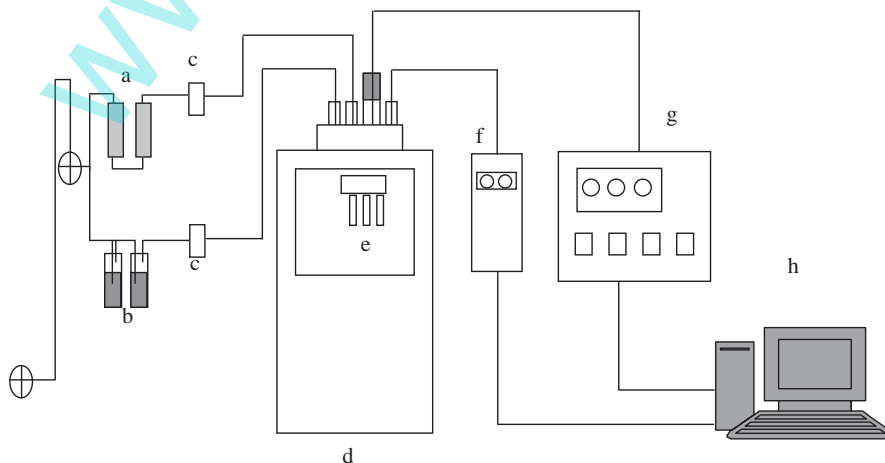


Fig. 3. Schematically plots the impedance measurement of sensors and the humidity atmosphere controller. (a) Molecular sieve and desiccating agent; (b) water; (c) mass flow controller; (d) controlled temperature detection chamber; (e) humidity sensor; (f) hygrometer; (g) LCZ meter; (h) PC.

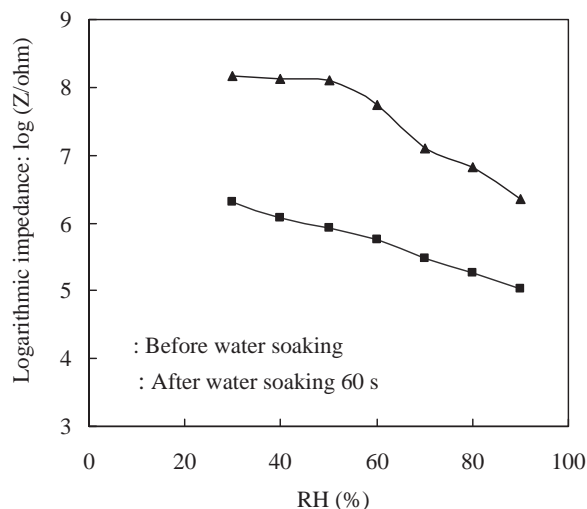


Fig. 4. Impedance versus relative humidity for humidity sensor made by spin-coating partially reduced GO film on PET substrate before and after soaking in water.

of 1 kHz, an applied voltage of 1 V, an ambient temperature of 25 °C. A frequency range of 50 Hz to 100 kHz, an RH range from 30 to 90% at 25 °C and an applied voltage of 1 V were used in the complex impedance analysis. 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 [33]. The RH values were measured using a calibrated hygrometer (Rotronic) with an accuracy of $\pm 0.1\%$ 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. Characterization of LBL covalently anchored and in-situ reduction of GO film

The stability in water of the flexible humidity sensor that was made by spin-coating partially reduced GO film on a PET substrate was investigated. Fig. 4 plots the logarithmic impedance ($\log Z$) of the flexible humidity sensor versus RH before and after soaking in water for 60 s. Clearly, a deviation in impedance was observed because the film peeled from the substrate. To solve the problem of the failure of the partially reduced GO film to be anchored on a PET substrate, the LBL was combined with a peptide chemical protocol. Fig. 1 shows the layer-by-layer procedure for covalently anchoring GO onto the thiol-modified gold electrode and then reducing it in-situ using conventional peptide chemical protocols. Firstly, the CH monolayer was chemisorbed onto the gold electrode surface, forming a gold–thiolate bond. Then, GO was covalently anchored to the surface of the CH-modified gold electrode by forming a peptidic bond: the carboxylic acid groups in the GO were activated by EDC/NHS (peptide coupling reagent), which reacted with amine groups in the CH-modified gold electrode to form chemical amide bonds. Finally, the covalently GO–CH-modified electrode

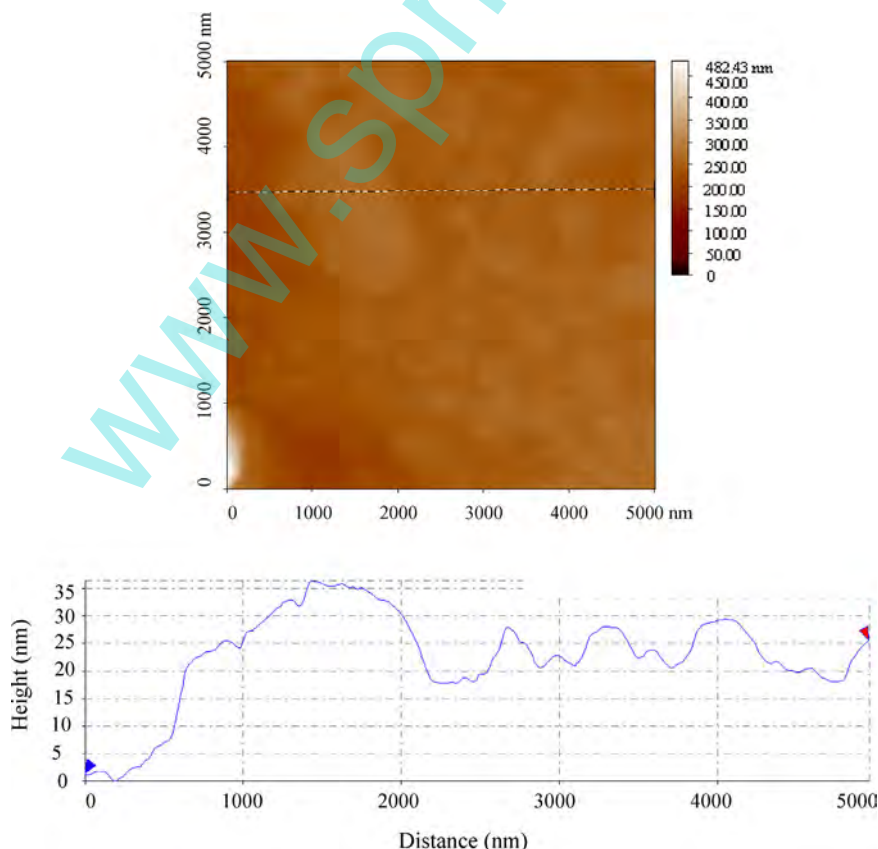


Fig. 5. AFM image of LBL covalently anchored partially reduced GO film.

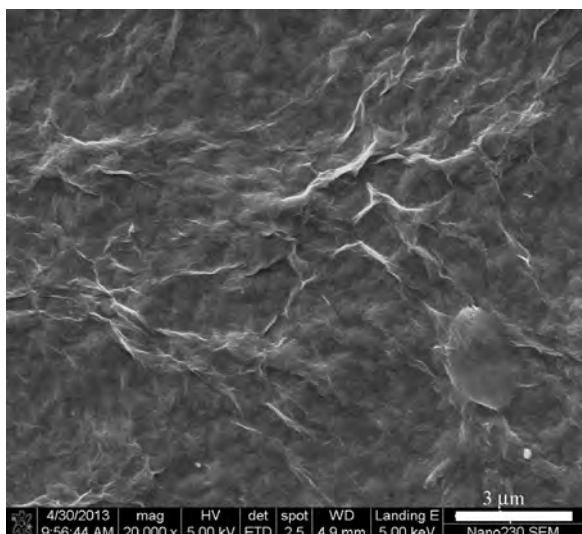


Fig. 6. FE-SEM image of LBL covalently anchored partially reduced GO film.

was partially reduced in-situ by NaBH_4 to yield partially reduced GO-CH/Au electrode (RGO-CH/Au).

3.1.1. Microstructure of surface

The surface morphology of the LBL covalently anchored partially reduced GO film was investigated by AFM. Fig. 5 shows the AFM of the LBL covalently anchored partially reduced GO film on a PET substrate. The root mean square (RMS) roughness of the LBL anchored partially reduced GO film was 20.6 nm. AFM analysis revealed that its thickness was 20–35 nm. Fig. 6 shows the SEM image of the film on a PET substrate. Clearly, multi-layered partially reduced GO with a flakelike and wrinkled structure was covalently anchored onto the substrate.

3.1.2. IR spectra

The GO film that was covalently anchored onto the CH/Au surface were investigated by IR spectroscopy. In Fig. 7, the IR spectrum of the GO that was covalently anchored onto the CH/Au surface included a peak at 3350 cm^{-1} attributable to the O–H stretching

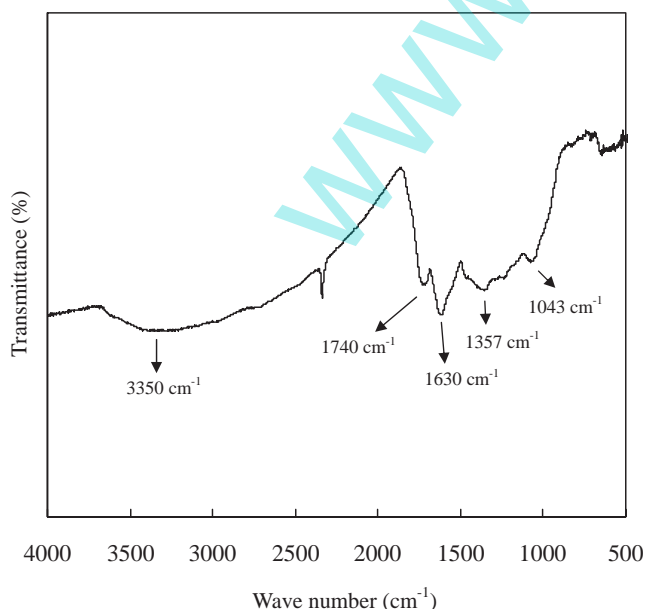


Fig. 7. IR spectra of GO covalently anchored onto CH/Au surface.

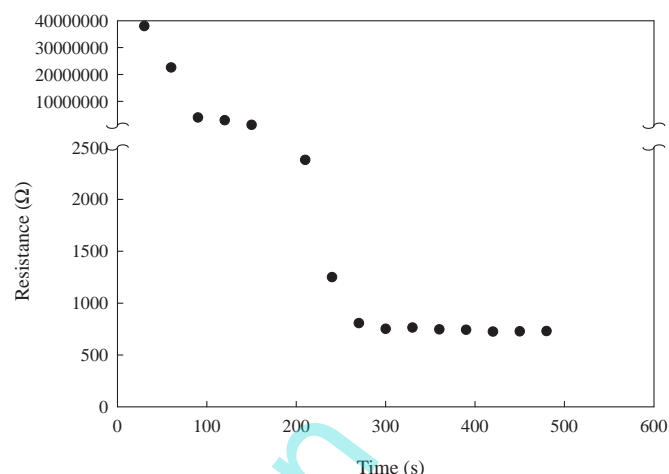


Fig. 8. Effect of reduction time on resistance of LBL covalently anchored GO film.

vibration, peaks at 1740 and 1630 cm^{-1} attributable to the C=O stretching vibrations, and a peak at 1357 cm^{-1} attributable to the deformation of O–H. Additionally, a peak at 1043 cm^{-1} was associated with amide (C–N) stretching in the GO that was covalently anchored onto the CH/Au surface. These results confirm that the GO was successfully covalently anchored onto the CH/Au surface.

3.1.3. Effect of reduction time on resistance of LBL covalently anchored GO film

Fig. 8 plots the effect of the reduction time on the resistance of the LBL covalently anchored GO film. The as-prepared LBL covalently anchored GO film exhibited a high resistance of about $35\text{ M}\Omega$ owing to the oxygen functional groups in its basal plane and edges. After reduction in NaBH_4 solution for 180 s, the LBL covalently anchored GO film was partially reduced and its resistance fell to $\sim 3\text{ M}\Omega$. As the reduction time increased to 300 s, the resistance of the LBL covalently anchored GO film decreased further to $\sim 750\ \Omega$; thereafter the resistance barely changed because all of the oxygen-containing functional groups had been eliminated [34]. These results clearly suggest that the GO was reduced by NaBH_4 .

3.2. Electrical and humidity-sensing properties and flexibility of sensor made of LBL covalently anchored reduced GO film

3.2.1. Effect of reduction time on electrical and humidity-sensing properties of sensor made of LBL covalently anchored reduced GO film

Fig. 9 plots the effect of reduction time on the impedance of the LBL covalently anchored reduced GO films as a function of relative humidity, and Table 1 summarizes the results of sensitivity (defined as the slope of logarithmic impedance ($\log Z$) versus %RH) and linearity (a correlation coefficient defined as the R -squared

Table 1
Sensitivity and linearity of LBL covalently anchored reduced GO-based flexible humidity sensors after various periods of reduction.

Reduced time (min)	Sensing curve	
	Sensitivity ($\log Z/\%RH$) ^a	Linearity (R^2) ^b
0	−0.0178	0.9666
1	−0.0354	0.9775
3	−0.0423	0.9951
5	−0.0005	0.9969

^a Sensitivity was defined as the slope of the logarithmic impedance versus relative humidity plot in the range 30 to 90% RH.

^b Linearity was shown as the correlation coefficient of the logarithmic impedance versus relative humidity plot in the range 30 to 90% RH.

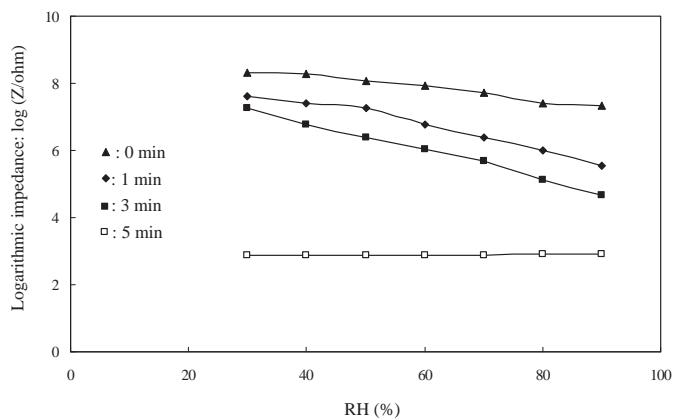


Fig. 9. Impedance versus relative humidity for LBL covalently anchored reduced GO film with various reduced time, measured at 1 V, 1 kHz and 25 °C.

value of the linear fitting curve in the range from 30 to 90% RH. Measurements were made at 25 °C using an AC voltage of 1 V, at 1 kHz. The impedance decreased with increasing reduction time owing to the removal of oxygen functional groups (as described in Section 3.1.3). When the reduction time was less than 3 min, the LBL covalently anchored GO film was partially reduced, and the impedance decreased with increasing humidity in the range 30–90% RH. The sensitivity and linearity of the sensor increased with the reduction time (Table 1). When the reduction time was 5 min, the LBL covalently anchored reduced GO film exhibited only a slight change in impedance with humidity in the range studied, undoubtedly because of its hydrophobic property and low resistance. The flexible humidity sensor that was made of LBL covalently

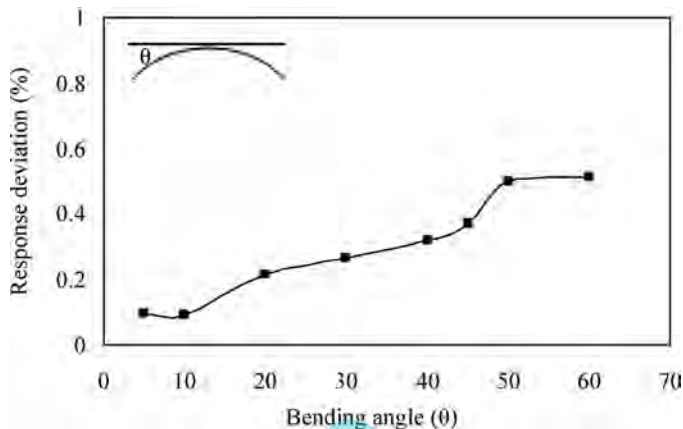


Fig. 11. Flexibility of LBL covalently anchored partially reduced GO film on PET substrate, measured at 1 V, 1 kHz and 25 °C.

anchored reduced GO film that has been reduced for 3 min was chosen for studying the water resistance, flexibility, humidity-sensing properties and sensing mechanism, because it exhibited the highest sensitivity and best linearity.

3.2.2. Water resistance

Fig. 10 plots the water resistance of the LBL covalently anchored partially reduced GO film. The impedance of the flexible sensor did not vary significantly when it was soaked in water for 5 min at the tested RH values of 30, 60, and 90%. This result reveals that the humidity sensor was sufficiently stable to endure soaking in water.

3.2.3. Flexibility properties

Fig. 11 plots the flexibility-related characteristics of the LBL covalently anchored partially reduced GO film that was used as a humidity sensor. The sensor response (S) was calculated

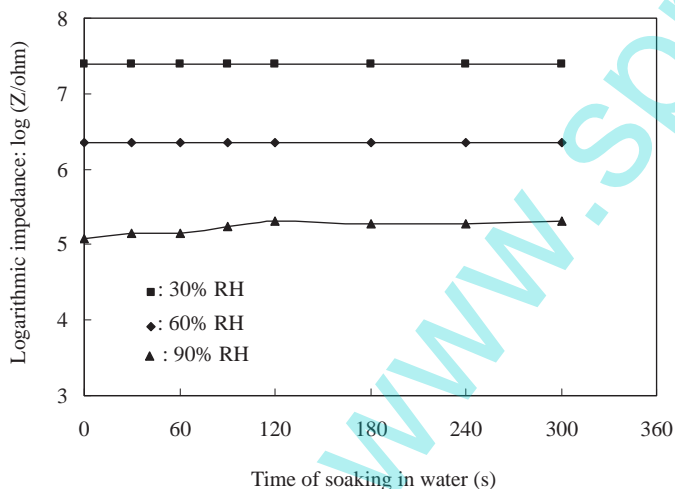


Fig. 10. Impedance versus relative humidity for LBL covalently partially anchored reduced GO film on PET substrate before and after soaking in water, measured at 1 V, 1 kHz and 25 °C.

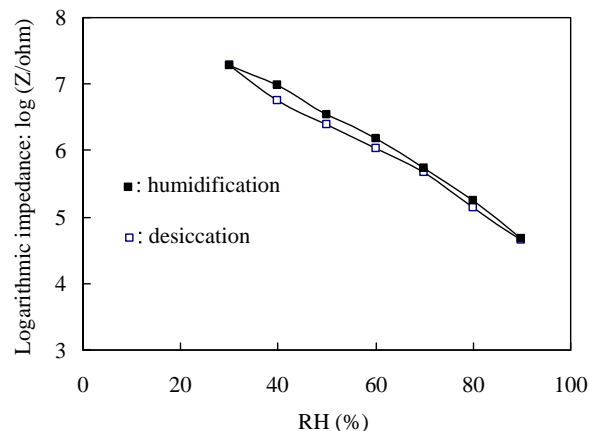


Fig. 12. Impedance versus relative humidity for LBL covalently anchored partially reduced GO film on PET substrate, measured at 1 V, 1 kHz and 25 °C.

Table 2

Flexible humidity sensor performance of this work compared with the literatures.

Sensor type	Fabrication method	Sensing material	Working range (% RH)	Sensitivity	Flexibility	Water resistance	References
Impedance-type	LBL-anchored ^a	Partially reduced GO	30–90	0.0423 log Z/%RH	Flexible	Yes	This work
QCM ^b -type	Spin-coating	GO	6.4–97.3	22.1 Hz/%RH	Rigid	No	[19]
Impedance-type	TBLI ^c	Reduced GO	10–90	6.3 Z/%RH	Flexible	No	[20]
Conductive-type	Drop-coating	Defect graphene	3–30	0.27–3.3%	Rigid	No	[21]
Stress-type	Spin-coating	Graphene oxide-silicon by-layer	10–98	79.3 μ V/%RH	Rigid	No	[22]

^a Layer-by-layer combined with a peptide chemical protocol.

^b Quartz crystal microbalance.

^c Two-beam-laser interference.

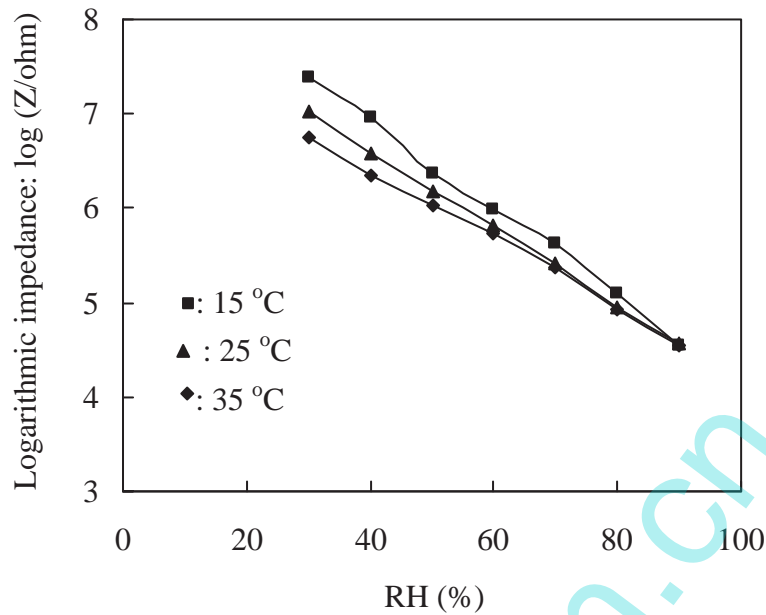


Fig. 13. Impedance versus relative humidity for LBL covalently anchored partially reduced GO film on PET substrate at various temperatures, measured at 1 V and 1 kHz.

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 transparent 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 <0.6%. These results reveal that even under an applied stress, the sensor remained highly flexible and it exhibited good electrical performance when it was bent.

3.2.4. Humidity-sensing properties

Fig. 12 plots the logarithmic impedance ($\log Z$) of the flexible 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 during humidification. In the range 30 to 90% RH, the impedance changed from 10^7 to $10^4 \Omega$ and the curves revealed a satisfactorily linear relationship ($Y = -0.0423X + 8.5228$;

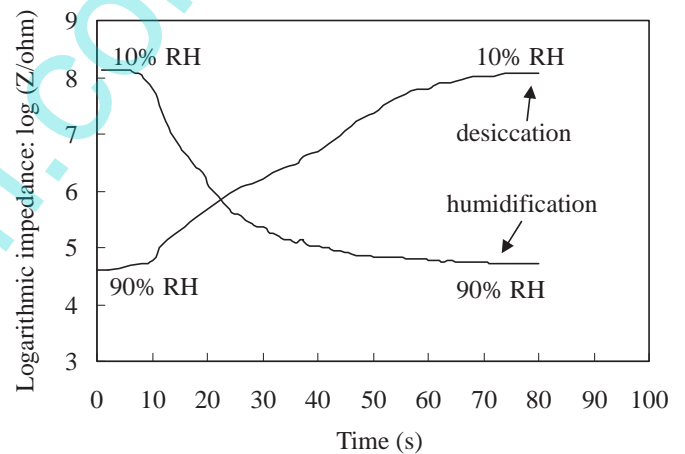


Fig. 15. Response-recovery properties of LBL covalently anchored partially reduced GO film on PET substrate, measured at 1 V, 1 kHz and 25 °C.

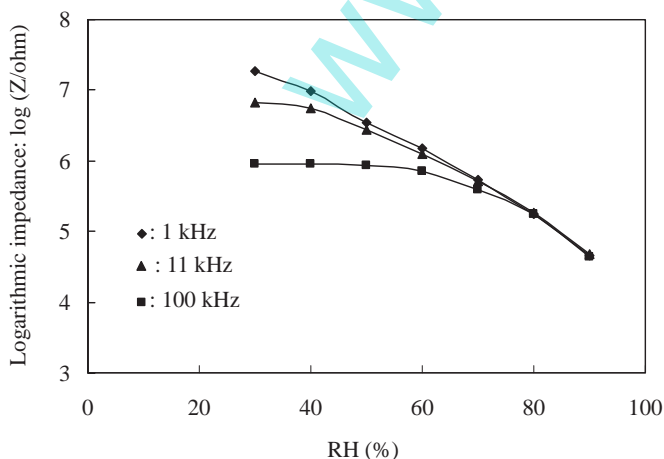


Fig. 14. Impedance versus relative humidity for LBL covalently anchored partially reduced GO film on PET substrate at various frequencies, measured at 1 V and 25 °C.

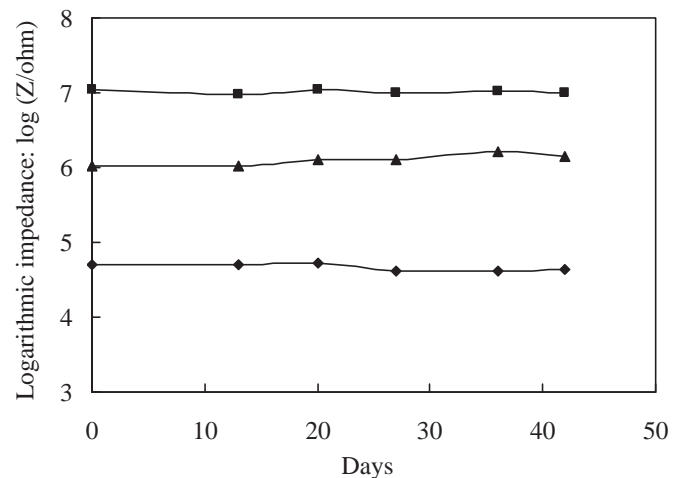


Fig. 16. Long-term stability of LBL covalently anchored partially reduced GO film on PET substrate, measured at 1 V, 1 kHz and 25 °C. (■) 30% RH; (▲) 60% RH; (◆) 90% RH.

$R^2 = 0.9951$) between logarithmic impedance ($\log Z$) and RH. The hysteresis (between humidification and desiccation, measured over an RH range of 30–90% RH) was less than 2.5% RH. Fig. 13 plots the logarithmic impedance ($\log Z$) of the flexible 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 $-0.39\% \text{ RH}/^\circ\text{C}$ over the humidity range 30–90% RH. Fig. 14 plots the logarithmic impedance ($\log Z$) of the flexible 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 flexible 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. 15 plots the response and recovery of the flexible humidity sensor that was measured at 25 °C and 1 kHz. The response time ($T_{\text{res},95\%}$) is defined as the time required for the impedance of the sensor to change by 95% of the maximum change following humidification from 10 to 90% RH. The recovery time ($T_{\text{rec},95\%}$) is defined as the time required for the sensor to recover 95% of the maximum change in impedance after desiccation from 90 to 10% RH. The response time ($T_{\text{res},95\%}$) and recovery ($T_{\text{rec},95\%}$) time of the sensor were 28 and 48 s, respectively. Fig. 16 plots the long-term stability. The flexible sensor impedance did not significantly vary for at least 42 days at the tested RH values of 30, 60, and 90% RH. Table 2 compares the humidity sensing properties of the presented flexible humidity sensor with those of sensors in the literature [19–22]. The flexible humidity sensor that was developed herein was water resistance because the reduced GO film was successfully anchored onto the CH/Au surface using the traditional peptide chemical protocol. The flexibility of the flexible humidity sensor that made of an LBL covalently anchored partially reduced GO film were greater than that of the sensor that was made of the reduced GO film grown by two-beam-laser interference technique.

3.3. Sensing mechanism of sensor made of LBL covalently anchored partially reduced GO film

Impedance spectroscopy is a powerful method for elucidating the conduction mechanisms of humidity sensors. Therefore, the obtained impedance plots were used to elucidate the transport of ions as a mechanism of conduction in the LBL covalently anchored partially reduced GO film on PET substrate. The complex impedance spectra of the sensor made of LBL covalently anchored partially reduced GO film at 30 and 90% RH are shown in Fig. 17. The impedance measurements were made in a frequency range from 50 Hz to 100 kHz, an AC voltage of 1 V and 25 °C. At 30% RH, a semicircular plot of film impedance was obtained. The film can be modeled as an equivalent parallel circuit that consists of a resistor and a capacitor [35–37]. When RH is increased to 90%, a semicircle (at high frequencies) that is connected to a straight line (at low frequencies) is observed. The LBL covalently anchored

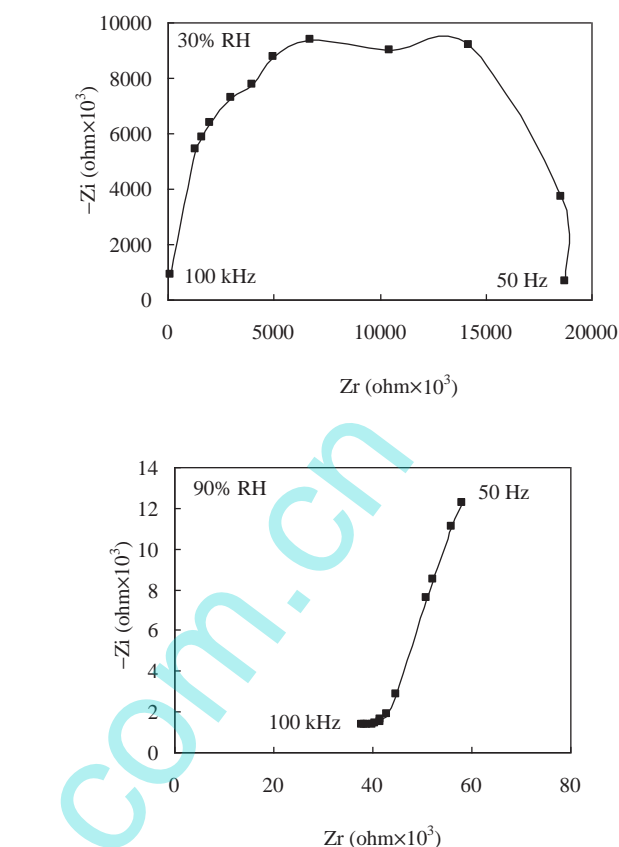


Fig. 17. Complex impedance plots of LBL covalently anchored partially reduced GO film on PET substrate at 30 and 90% RH.

partially reduced GO film adsorbed more water molecules so the impedance of the film was low and the semicircle was small. The straight line at low frequencies arose from the diffusion of ions (H_3O^+) across the interface between the electrode and the partially reduced GO film. Therefore, the following model (shown in Fig. 18) applies. First, when the relative humidity (RH) is low (<30% RH), little water vapor is adsorbed on reduced GO film, forming a dipole layer with the negative charges toward the reduced GO. Reduced GO film is well known to exhibit the electrical behavior of a p-type semiconductor. The water vapor behaves like as an oxidant (electron-acceptor), significantly increasing the electrical conductivity in the LBL covalently anchored partially reduced GO film [38–43]. Second, when the RH is further increased, water molecules are physisorbed in multilayers on the surface of the LBL covalently anchored partially reduced GO film, forming H_3O^+ ions by dissociation. Therefore, the increase in conductivity of the LBL covalently anchored partially reduced GO film is believed to have been caused

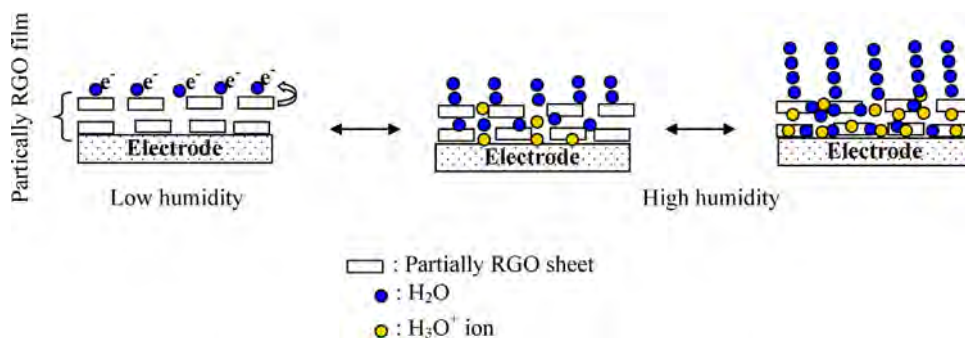


Fig. 18. Response of LBL covalently anchored partially reduced GO film on PET substrate to humidity.

by ions at high RH (Fig. 17) [44,45]. The generally sensing principle of the LBL covalently anchored partially reduced GO film is based on electronic and ionic conductivity at the low and high RH, respectively.

4. Conclusions

A novel flexible humidity sensor was successfully fabricated by the LBL covalent anchoring of a GO film, which is then reduced *in situ* to a partially reduced GO film, on a modified PET substrate. Microstructural observations revealed that a multi-layered flake-like RGO film was covalently anchored onto the PET substrate. The flexible humidity sensor had high flexibility ($D < 0.6\%$) when it was bent downward at an angle of up to 60° . This flexible humidity sensor was sufficiently stable to endure soaking in water, it exhibited good sensitivity and acceptable linearity ($Y = -0.0423X + 8.5228$; $R^2 = 0.9951$) between logarithmic impedance ($\log Z$) and RH in the range 30 to 90% RH, negligible hysteresis (within 2.5% RH), a short response time (28 s) and recovery time (48 s), and good long-term stability (42 days at least), measured at 1 V, 1 kHz and 25°C . The flexible humidity sensor's linearity depended on the applied frequency. The temperature influence between 15 and 35°C ; found to be -0.39% RH/ $^\circ\text{C}$ for 30 to 90% RH. The plots of the complex impedance of the LBL covalently anchored partially reduced GO film revealed that the curves changed from semicircular at 30% RH to linear at 90% RH. These results reflect the contribution of ions to the conductivity of the LBL covalently anchored partially reduced GO film at high humidity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2014.04.035>.

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