



# Low-humidity sensing properties of carboxylic acid functionalized carbon nanomaterials measured by a quartz crystal microbalance



Pi-Guey Su\*, Xian-Ren Kuo

Department of Chemistry, Chinese Culture University, Taipei 111, Taiwan

## ARTICLE INFO

### Article history:

Received 29 August 2013

Received in revised form 21 October 2013

Accepted 22 October 2013

Available online 12 November 2013

### Keywords:

Low-humidity sensing

Quartz crystal microbalance

MWCNT-COOH

GO

Adsorption dynamic analysis

## ABSTRACT

Low-humidity sensing performance of raw multi-walled nanotubes (MWCNTs), graphene and carboxylic acid functionalized MWCNTs (MWCNT-COOH) and graphene (GO) thin films were investigated by using a quartz crystal microbalance (QCM). The characterizations of the thin films were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Water vapor molecules adsorbed onto the GO thin film had a larger frequency shift than the MWCNT-COOH thin film (especially at low humidity levels). Adsorption dynamic analysis, molecular mechanics calculation (association constant), was applied to elucidate how amounts of surface functionalized groups (–COOH) of MWCNTs and graphene increase the sensitivity to low-humidity.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Considerable consumer demand persists for reliable and accurate humidity sensors, especially for use under low-humidity conditions, in meteorological, agricultural, clinical, and biotechnological fields and for manufacturing applications [1]. New methods and materials are sought to improve existing sensors and detect the lowest humidity levels with increased accuracy.

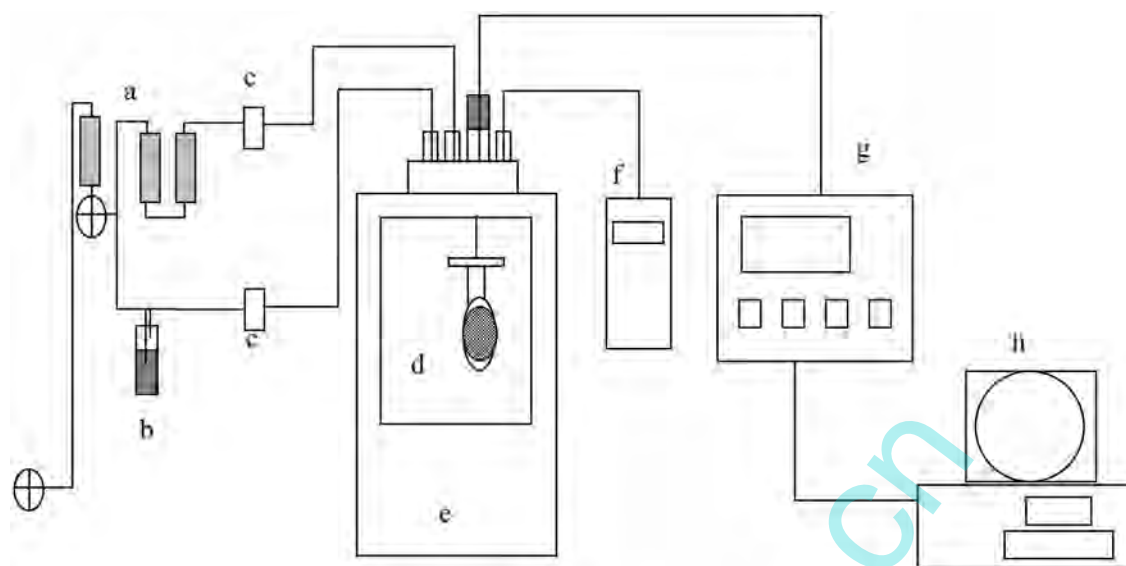
Different sensing approaches, including impedance, capacity [2], optic [3], photonic crystal fiber [4–6], field effect transistors (FETs) [7,8], surface acoustic wave (SAW) [9] and quartz crystal microbalance (QCM) [10–12], have been adopted to detect humidity. Among these sensing technologies for humidity detection, the QCM is a very stable device, capable of determining an extremely small mass changes [13]. Therefore, QCM-based sensors may be a promising solution for detecting low levels of humidity. A hygroscopic material was coated on the quartz crystal to increase the sensor's sensitivity by adsorption of water from the humidity of the ambient air. According to Sauerbrey equation, the extra mass causes a resonance frequency shift  $\Delta f$  (Hz) equal to [14]:

$$\Delta f = \left( -2.3 \times 10^{-6} \frac{f_0^2}{A} \right) \Delta m \quad (1)$$

where  $f_0$  (MHz) denotes the basic frequency of the unloaded piezoelectric crystal,  $A$  (cm<sup>2</sup>) represents the surface area of the electrode, and  $\Delta m$  (g) is the change in mass on the crystal surface. Therefore, the performance characteristics of QCM-based sensors primarily depend on the chemical nature and physical properties of the coating materials.

Nanosized materials were used for detection of gases owing to their high surface area and availability of many active sites; therefore, more and more research groups put in their effort to develop highly sensitive nanomaterials, such as nanosized zeolite films [15], ZnO nanostructure films [16], TiO<sub>2</sub> nanowires/poly(2-acrylamido-2-methylpropane) sulfonate [17] and polypyrrole/TiO<sub>2</sub> nanoparticles (PPy/TiO<sub>2</sub> NPs) [18]. Among the different nanomaterials one could consider for developing a gas sensor, carbon nanomaterials have been attracting a great deal of interest. Carbon materials with inherent nanoscale features have potential for becoming ideal components for sensor technology, because of combining excellent detection sensitivity with interesting transduction properties [19]. Carbon nanotubes (CNTs) have emerged as a new class of one-dimensional structure having extra ordinary electrical and mechanical properties [20]. CNTs have attracted considerable interest for demanding applications in the field of gas sensing due to their high surface areas provided by their central hollow cores and outside walls for gas adsorption in the presence of different gases at low concentrations [21,22]. Graphene is composed of a two-dimensional (2D) array of carbon atoms that are covalently connected via sp<sup>2</sup> bonds to form a honeycomb sheet [23]. Graphene have been widely used in batteries, supercapacitors, nanoelectronic and electrochemical sensors because of its high mechanical

\* Corresponding author. Tel.: +886 2 28610511x25332; fax: +886 2 28614212.  
E-mail addresses: [spg@faculty.pccu.edu.tw](mailto:spg@faculty.pccu.edu.tw), [spg@ulive.pccu.edu.tw](mailto:spg@ulive.pccu.edu.tw) (P.-G. Su).



**Fig. 1.** Schematic diagram of experimental set-up for the QCM sensor measurement and low humidity atmosphere controller. (a) Molecular sieve and desiccating agent; (b) water; (c) mass flow controller; (d) detecting chamber and QCM; (e) thermostat; (f) low humidity hygrometer; (g) oscillator and frequency counter; (h) PC.

strength, high surface area, high electron mobility at room temperature and low manufacturing cost [23–25]. Therefore, CNTs-based and graphene-based materials have been fabricated as relative humidity sensors [26–29]. Zhu et al. fabricated a relative humidity sensor that by coating multi-walled CNTs (MWCNTs) that were treated by ball milling and the hydrogen plasma technique on a QCM [26]. Yao et al. fabricated a relative humidity sensor that by coating graphene oxide (GO) on a QCM [27]. Zeng et al. fabricated a resistive-type humidity that was made of defect graphen [28]. Sun et al. fabricated a flexible humidity sensor that by two-beam-laser interference reduction and patterning of GO [29]. Recently, CNTs and their nanocomposites materials were prepared as films coated on an electrode of QCM to detect low-humidity in our previous studies [30–32]. These materials included carboxylic acid functionalized MWCNTs (MWCNT-COOH) [30], single-walled carbon nanotube/Nafion composite material (SWCNTs/Nafion) [31,32] and multi-walled carbon nanotube/Nafion composite material (MWCNTs/Nafion) [32]. However, no attempt has been made to fabricate the QCM-based low-humidity sensor based on graphene and GO. In this study, raw MWCNTs, MWCNT-COOH, graphene and GO were used to construct QCM-based low-humidity sensors. The low-humidity sensing properties of GO coated on the QCM was compared with that of MWCNT-COOH coated on the QCM. This study investigates how the functional groups on CNTs and graphene and low-humidity sensing properties are related, and it emphasizes the most important properties associated with sensitivity. Furthermore, the adsorption dynamics of water vapor molecules onto MWCNT-COOH and GO thin films coated on the QCM and the functional groups and microstructure of CNT and graphene were employed to elucidate the sensing properties (sensitivity).

## 2. Experimental

### 2.1. Low-humidity sensor fabrication

#### 2.1.1. Sensing materials

The MWCNT-COOH dispersion was prepared using the well-established acid treatment [33] of raw chemical vapor deposition (CVD) grown MWCNTs (200 mg, Sunnano Inc.) using an  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture (3:1, 50 mL) and sonicated at 60 °C for 24 h, after which the acid mixture was decanted. The residue was

subsequently re-suspended in deionized water and centrifuged at 10,000 rpm for 30 min. This process was repeated several times until the solution pH was neutral and was sonicated to facilitate stable suspension of MWCNT-COOH in aqueous media. Graphene (99.9%, UniRegion Bio-Tech) and Graphene oxide (GO; 5 g/L, UniRegion Bio-Tech) were used without further purification.

#### 2.1.2. Fabrication of the QCM electrodes

The AT-cut quartz crystals with a fundamental resonance frequency of 10 MHz were obtained from ANT Technologies Corp., Taiwan. The gold electrode of the QCM was rinsed in deionized water and then cleaned ultrasonically in acetone. Following drying, both sides of the QCM electrode were coated with the mixture precursor solution by spin coating at a rate of 2000 rpm for 120 s. Consequently, raw MWCNTs, MWCNT-COOH, graphene and GO thin films had mass values 0.858, 0.749, 0.600 and 1.732  $\mu\text{g}$ , respectively, on the QCM disk. Unless otherwise stated, all measurements were taken at room temperature, around  $23.0 \pm 1.5$  °C.

### 2.2. Instruments and analysis

As shown in Fig. 1, a divided humidity generator was used as the principal facility for producing the testing gases. The required water vapor concentration 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 and flow display power-supply used is the Protec PC-540 manufactured by Sierra Instruments Inc. The lowest testing point is limited by the dryness of the gas. A low-humidity hygrometer (HYGROCLIP IC-3, Rotronic Inc.) which measurement range and precision are 0–100% RH and 0.1% RH, respectively, and was used as reference standard hygrometer to measure the testing water vapor concentration produced by the divided flow humidity generator. QCM sensors were connected to an outlet of the divided flow humidity generator and calibrated by the reference standard hygrometer. The setting volume ratio of the moist air and temperature would be adjusted according to the reading of the low-humidity hygrometer calibrated at the CMS/NML (Center for Measurement Standards/National Measurement Laboratory)

humidity laboratory. The volume ratio of the moist air was calculated by the following equation:

$$\text{ppm}_v (\mu\text{L/L}) = \frac{V_v}{V} \times 10^6 \quad (2)$$

where  $V_v$  is the volume of water vapor and  $V$  is the total volume. Measurement procedures were recorded as below: firstly the synthetic dry air was passed through the detection chamber until the deviation of the frequency of QCM was within 2 Hz/s and then the required water vapor concentration was flowed into the detection chamber, finally the synthetic dry air was passed through the detection chamber until the frequency of QCM recovered to its initial value. The initial volume ratio of the moist air was 2.77 ppm<sub>v</sub> for all experiments. All the measurements were performed at the room temperature  $23.0 \pm 1.5^\circ\text{C}$  and controlled by the thermostat. An infrared spectrometer (Nicolet 380) was used to obtain the IR spectra of the MWCNT-COOH and GO films. The surface microstructure and morphology of the thin film that was coated on a QCM electrode were 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 carboxyl-functionalized MWCNTs and graphene were quantitatively analyzed by back titration to determine the carboxylic acid concentrations on the surface of MWCNTs and graphene.

### 3. Results and discussion

#### 3.1. Surface microstructure characteristics of MWCNT-COOH and GO thin films

Fig. 2 presents the SEM images of MWCNT-COOH and GO thin films. Fig. 2(a) shows the surface microstructure of the MWCNT-COOH mat coated on the QCM. Many small and irregular pores were observed due to their random entanglement and alignment in nanotubes. Fig. 2(b) presents the surface microstructure of the GO coated on the QCM. Clearly, GO thin film with a flakelike and wrinkled structure was observed.

The surface morphology and uniformity of CNT thin films were investigated by AFM. Fig. 3(a) and (b) shows the surface topography of  $5 \mu\text{m} \times 5 \mu\text{m}$  MWCNT-COOH and GO thin films, respectively, coated on the QCM. The data of the root mean square (RMS) roughness of MWCNT-COOH and GO thin films was 25.5 and 12.3 nm, respectively. Fig. 3(a) shows large amounts of granules on the QCM. GO thin film had a smoother surface film than that of MWCNT-COOH thin film (Fig. 3(b)).

#### 3.2. IR spectra of MWCNT-COOH and GO thin films

The raw MWCNTs and graphene that were treated with acid, were analyzed using an FTIR spectrometer, as presented in Fig. 4(a) and (b), respectively. The IR spectra of the MWCNT-COOH and GO both exhibited a peak at  $3350 \text{ cm}^{-1}$  attributable to the O–H stretching vibration, a peak at  $1740 \text{ cm}^{-1}$  attributable to the C=O stretching vibrations (carboxylic group) and a peak at  $1620 \text{ cm}^{-1}$  attributable to the asymmetric stretching vibration of the anion carboxylate ( $-\text{COO}^-$ ) and stretching of the C=C bond [33,34]. These results confirm that the carboxyl groups were functionalized on the surface of the raw MWCNT and graphene. Moreover, chemical functional groups,  $-\text{COOH}$ , have an important role in low-humidity sensing.

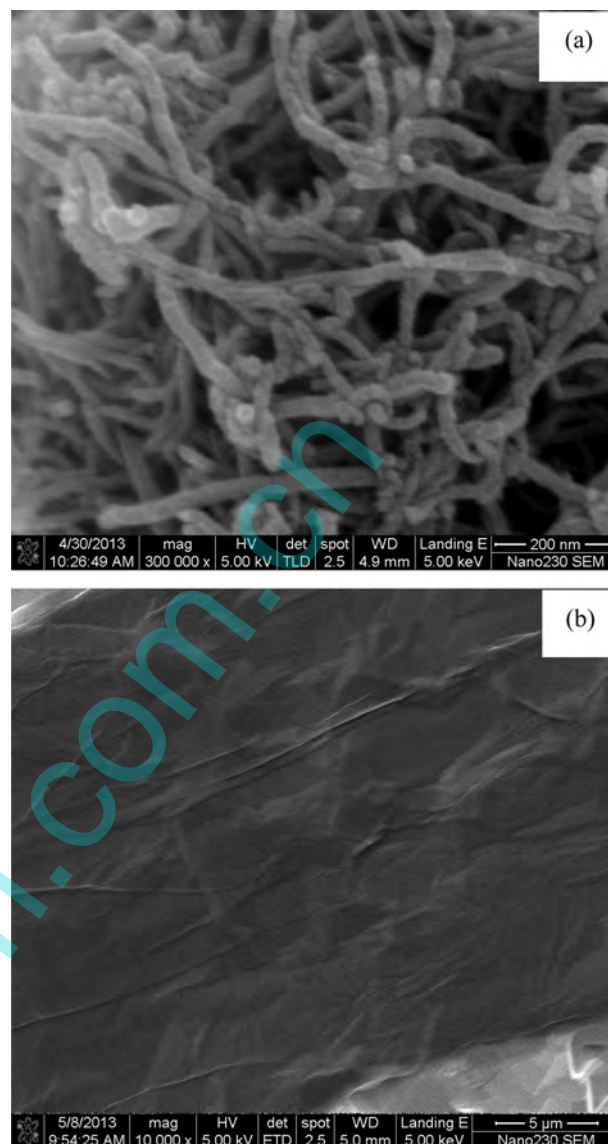


Fig. 2. FE-SEM micrographs of (a) MWCNT-COOH and (b) GO thin films.

#### 3.3. Low-humidity sensing properties of raw MWCNTs, MWCNT-COOH and graphene and GO thin films

Fig. 5 plots the frequency shifts of raw MWCNTs, MWCNT-COOH, graphene and GO thin films as a function of time for various volume ratios of moist air in the range of 345–11,516 ppm<sub>v</sub>. The frequency shifts of raw MWCNTs, MWCNT-COOH, graphene and GO thin films were normalized to the mass of the coated sensing materials. The normalized frequency shifts of the MWCNT-COOH and GO thin films were higher than those of raw MWCNTs and graphene thin films because that CNTs and graphene are known to be highly hydrophobic. Additionally, the normalized frequency shifts of the GO thin film were higher than that of MWCNT-COOH thin film, especially at low levels of humidity (<9744 ppm<sub>v</sub>). Therefore, MWCNT-COOH and GO thin films were further investigated for evaluation their low-humidity sensing characterizations.

Table 1 lists the corresponding sensitivities for MWCNT-COOH and GO thin films. The results of calibration curve of MWCNT-COOH and GO thin films are plotted in Fig. 6 and the slope and linear correlation coefficient ( $R^2$ ) were calculated as shown in Table 2. When the volume ratio of moist air was 345 ppm<sub>v</sub>, the sensitivity of MWCNT-COOH and GO thin films was 0.0267 and 0.0386,

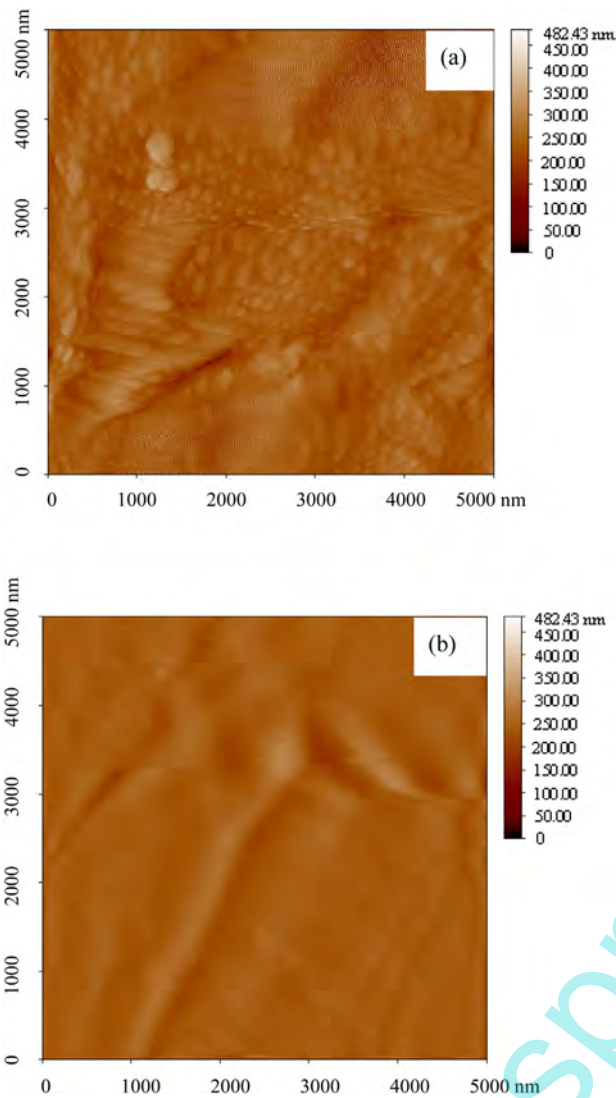


Fig. 3. AFM micrographs (5 μm × 5 μm) of (a) MWCNT-COOH and (b) GO thin films.

respectively (Table 1), demonstrating that the response of the GO thin film was higher than that of the MWCNT-COOH thin film, especially at low levels of humidity (<9744 ppm<sub>v</sub>). However, when the volume ratio of moist air was above 9744 ppm<sub>v</sub>, the sensitivity of MWCNT-COOH thin film was higher than that of GO thin film. For GO thin film, the linear sensing characteristics at the ranges

**Table 1**  
Sensitivity to humidity of MWCNT-COOH and GO thin films coated on QCM for different volume ratios of moist air.

Δppm <sub>v</sub> <sup>b</sup>	Sensitivity <sup>a</sup>	
	MWCNT-COOH	GO
345	0.0267	0.0386
2068	0.0108	0.0155
3313	0.0086	0.0119
4229	0.0080	0.0102
5295	0.0078	0.0091
6740	0.0070	0.0079
7612	0.0069	0.0075
9744	0.0068	0.0066
11,516	0.0064	0.0060

<sup>a</sup> The sensitivity of the various sensing films was defined as  $\frac{-\Delta f}{\Delta \text{ppm}_v \times \mu\text{g}}$ .

<sup>b</sup> The Δppm<sub>v</sub> was defined as the volume ratio subtracted by the initial volume ratio of moisture air (2.77 ppm<sub>v</sub>).

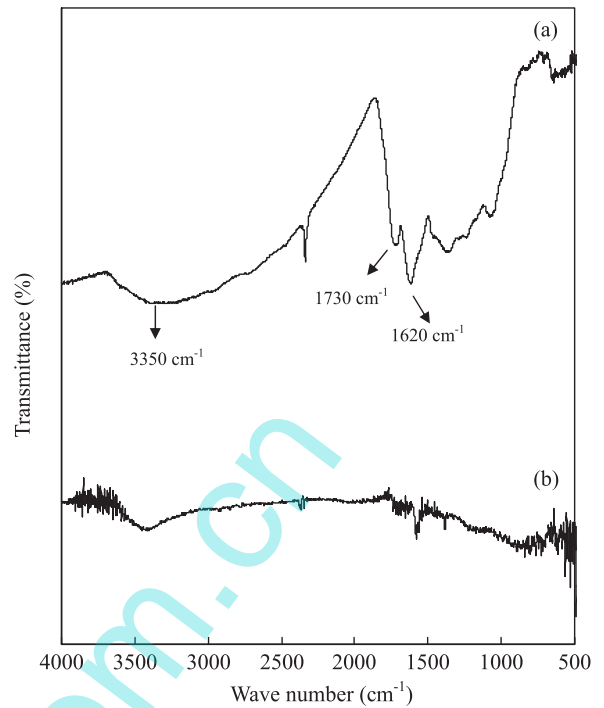


Fig. 4. IR spectra of (a) GO and (b) MWCNT-COOH thin films.

of 345–3313 and 3313–11,516 ppm<sub>v</sub> show different performance. The steep decrease in slope was observed at the volume ratio of moist air of 3313–11,516 ppm<sub>v</sub> (Table 2).

As described in Section 3.1, the MWCNT-COOH thin film had rougher surface than that of GO thin film. Therefore, the fact that the response of the GO thin film was higher than that of the MWCNT-COOH thin film, especially at low levels of humidity, was not related to surface morphology. The issue can be analyzed by considering the functional groups on CNTs and graphene. The presence of COOH groups sites on the MWCNTs and graphene form low-energy adsorption sites that also serve as nucleation sites for analyte condensation. Therefore, the MWCNT-COOH and GO thin film had higher sensitivity to low-humidity than that of raw MWCNTs and graphene, which was attributed to the fact that water vapor was preferentially adsorbed on polar oxygen-containing defects (COOH) via the formation of hydrogen (H) bonds [27,35,36]. From the results of back titration of the functionalized MWCNTs

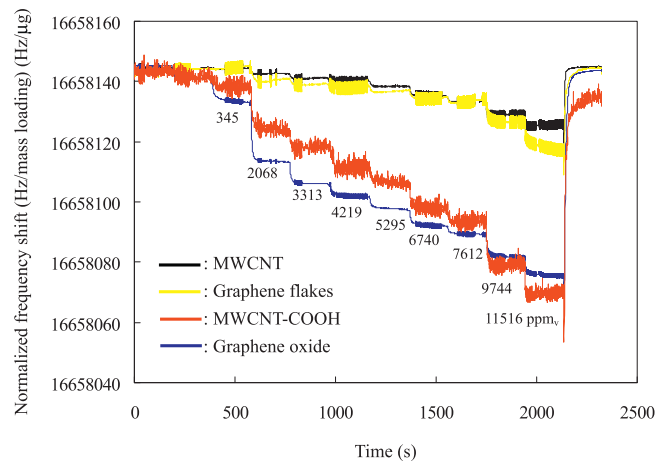
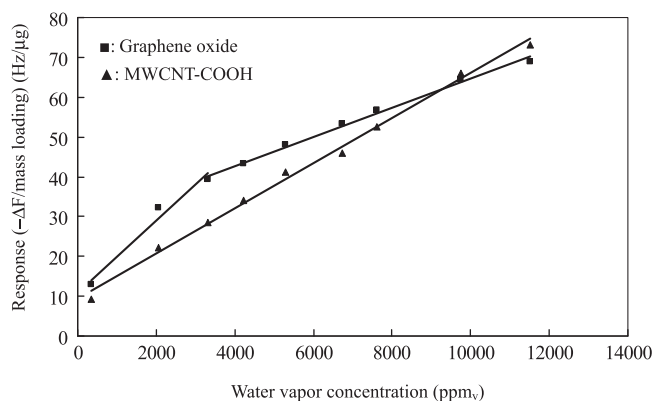


Fig. 5. Normalized frequency shifts (Hz/μg) as a function of time (s) for different volume ratio of the moist air on raw MWCNTs, MWCNT-COOH, graphene and GO thin films.

**Table 2**  
Linear sensing characteristics of MWCNT-COOH and GO thin films coated on QCM at different volume ratio of moist air.

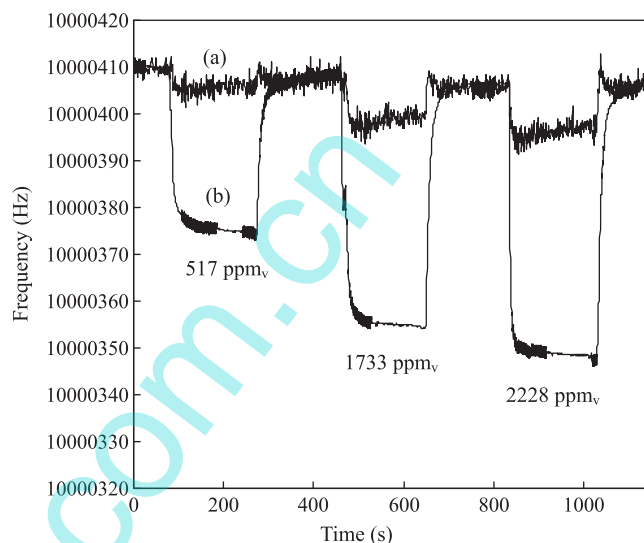
	Sensing characteristics			
	345–3313 ppm <sub>v</sub>		3313–11,516 ppm <sub>v</sub>	
	Slope	Linearity <sup>a</sup>	Slope	Linearity <sup>a</sup>
MWCNT-COOH	0.0066	0.9885	0.0055	0.9940
GO	0.0090	0.9744	0.0037	0.9942

<sup>a</sup> The linearity was defined as the linear regression coefficient of  $R^2$  – value of linear fitting curve.



**Fig. 6.** Response ( $-\Delta F/\mu\text{g}$ ) as a function of volume ratio (ppm<sub>v</sub>) for MWCNT-COOH and GO thin films.

and graphene, the COOH concentration on the surface of graphene (148.1 mmol/g) was higher than that of MWCNTs (2.1 mmol/g), and so had more sites for the adsorption of water molecules, and thereby improved the sensitivity of GO thin film than that of the MWCNT-COOH thin film at low levels of humidity (<9744 ppm<sub>v</sub>). But, at higher volume ratio of moist air (3313–11,516 ppm<sub>v</sub>), suggested the absence of active sites for reaction to occur and, hence,



**Fig. 7.** Reversibility of adsorption of water vapors on (a) MWCNT-COOH and (b) GO thin films.

[12,37] explained the increase in sensitivity to low-humidity of the MWCNT-COOH and GO thin films.

The time course of adsorption behavior at the experimental dilute concentration is expressed simply as the follows:



the steep decreased in slope was observed. The MWCNT-COOH thin film had rough surface and irregular pores (Figs. 2(a) and 3(a)). When at a low-humidity, few water vapor molecules accumulated around these pores; consequently, inducing capillary condensation is difficult [34]. Many water vapor molecules accumulated around these pores; consequently, inducing capillary condensation easily, and thereby the sensitivity of MWCNT-COOH thin film was higher than that of GO thin film at volume ratio of moist air above 9744 ppm<sub>v</sub> (Figs. 5 and 6).

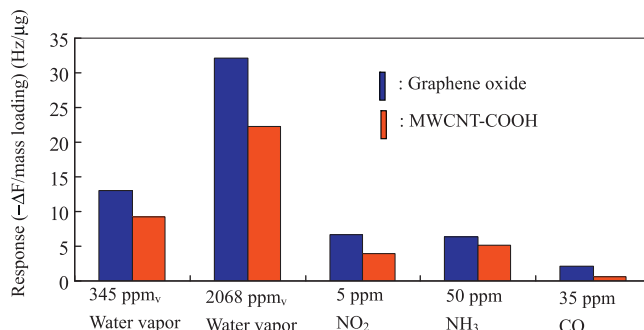
Fig. 7 plots the results of the adsorption/desorption of water vapors on the MWCNT-COOH and GO thin films at three testing points, 517, 1733 and 2228 ppm<sub>v</sub>. The adsorption and desorption of water on the MWCNT-COOH and GO thin films were reversible at three tested water vapor concentrations. Fig. 8 plots the results concerning the cross-sensitivity effects of NO<sub>2</sub>, NH<sub>3</sub> and CO gases on the MWCNT-COOH and GO thin films. NO<sub>2</sub>, NH<sub>3</sub> and CO gases may be regarded as having unobvious cross-sensitivity effects with water vapor molecules even at a low testing concentration of 345 ppm<sub>v</sub> of water vapor molecules.

#### 3.4. Adsorption properties of MWCNT-COOH and GO thin films

The adsorption behaviors of water vapor molecules by MWCNT-COOH and GO thin films were compared. The following reaction

where  $k_1$  and  $k_{-1}$  are adsorption and desorption rate constant, respectively. The amount of water vapor molecules,  $\Delta m_t$ , formed on the sensing films at time  $t$ , is then given by the following equations under Langmuir isotherm adsorption conditions [12,37]:

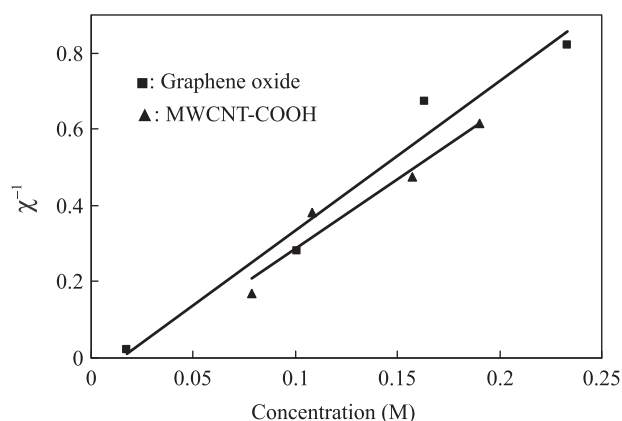
$$\Delta m_t = [\text{sensing films} - \text{water vapour molecules}]_t = \Delta m_\infty \left[ 1 - \exp\left(-\frac{t}{\chi}\right) \right] \quad (4)$$



**Fig. 8.** Response ( $-\Delta F/\mu\text{g}$ ) of GO and MWCNT-COOH thin films to various gases.

**Table 3**  
Kinetic parameters for adsorption and desorption of water vapor molecules onto MWCNT-COOH and GO thin films.

Films	Adsorption rate constant $k_1$ ( $M^{-1}s^{-1}$ )	Desorption rate constant $k_{-1}$ ( $s^{-1}$ )	Association constant $K$ ( $M^{-1}$ )
MWCNT-COOH	3.662	0.080	45.94
GO	3.923	0.056	70.05



**Fig. 9.** Linear plot of the reciprocal of relaxation time ( $\chi^{-1}$ ) against vapor concentration (M) for MWCNT-COOH and GO thin films.

$$\chi^{-1} = k_1[\text{water vapour molecules}] + K_{-1} \quad (5)$$

where  $\Delta m_{\infty}$  denotes the maximal amount of water vapor molecules adsorbed on the sensing films at  $t \rightarrow \infty$  and  $\chi$  is relaxation time. Adsorption time courses at different concentrations (0.0172–0.2329 M) were derived using Eqs. (4) and (5). Fig. 9 plots the linear correlation between reciprocal relaxation time ( $\chi^{-1}$ ) of adsorption and the concentration of water vapor on sensing films (MWCNT-COOH and GO). Fig. 6 and Eq. (5) yield the adsorption rate constant  $k_1$ , the desorption rate constant  $k_{-1}$  and the association constant  $K (=k_1/k_{-1})$  for water vapor on sensing films (Table 3). The GO–water vapor molecules had the largest  $k_1$  value. This experimental result coincides with the result, indicating that water vapor molecules are more easily adsorbed on GO than on MWCNT-COOH thin film. The association constant  $K$  of water vapor molecules onto the GO thin film was higher than that of MWCNT-COOH thin film. Therefore, the larger association constant ( $K = 70.05 M^{-1}$ ) of water vapor onto the GO thin film than onto the MWCNT-COOH thin film is associated with the larger adsorption rate constant and the smaller desorption rate constant. These results suggest that the adsorption of water vapor molecules on the amounts of functional groups (–COOH) on the surface of carbon-based nanomaterials plays a predominant role at low-humidity sensing. Therefore, the GO thin film was more sensitive to water vapor molecules than the MWCNT-COOH thin film at low levels of humidity (Table 1).

#### 4. Conclusion

The surface carboxylic acid functionalized MWCNTs and graphene can enhance the surface properties of MWCNTs and graphene and increase the sensitivity of MWCNTs and graphene to low levels of humidity. The amounts of surface functionalized groups (–COOH) of MWCNTs and graphene dominated the low-humidity sensing properties (especially at low humidity levels). The GO coated on the QCM electrode had high sensitivity (especially at low humidity levels) and acceptable linearity.

Based on the Langmuir isotherm adsorption assumption, the adsorption rate constant  $k_1$  for water vapor molecules on GO is

larger than that for MWCNT-COOH coated on QCM. Moreover, molecular mechanics calculations supported the experimental results, indicating that the high sensitivity of the GO thin film to water vapor molecules is ascribed to the slightly larger association constant  $K$  of the GO thin film to water vapor molecules than that of MWCNT-COOH thin film due to the COOH group sites formed on the surface of graphene.

#### Acknowledgements

The authors thank the National Science Council (grant no. NSC 100-2113-M-034-001-MY3) of Taiwan for support.

#### References

- [1] P.R. Story, D.W. Galipeau, R.D. Mileham, A study of low-cost sensors for measuring low relative humidity, *Sens. Actuators B* 24–25 (1995) 681–685.
- [2] Y. Sakai, Y. Sadaoka, M. Matsuguchi, Humidity sensors based on polymer thin films, *Sens. Actuators B* 35–36 (1996) 85–90.
- [3] P.R. Somani, A.K. Viswanath, R.C. Aiyer, S. Radhakrishnan, Charge transfer complex-forming dyes incorporated in solid polymer electrolyte for optical humidity sensing, *Sens. Actuators B* 80 (2001) 141–148.
- [4] S. Zhang, Y. Zhu, S. Krishnaswamy, Nanofilm-coated long-period fiber grating humidity sensors for corrosion detection in structural health monitoring, *Proc. SPIE* 7893 (2011) 79831A.
- [5] S. Zhang, Y. Zhu, S. Krishnaswamy, Nanofilm-coated photonic crystal fiber long-period gratings with modal transition for high chemical sensitivity and selectivity, *Proc. SPIE* 8346 (2012) 83460D.
- [6] S. Zhang, Y. Zhu, S. Krishnaswamy, Fiber humidity sensors with high sensitivity and selectivity based on interior nanofilm-coated photonic crystal fiber long-period gratings, *Sens. Actuators B* 176 (2013) 264–274.
- [7] S.P. Lee, K.J. Park, Humidity sensitive field effect transistors, *Sens. Actuators B* 35–36 (1996) 80–84.
- [8] A. Star, T.-R. Han, V. Joshi, J.R. Stetter, Sensing with Nafion coated carbon nanotube field-effect transistors, *Electroanalysis* 16 (2004) 108–112.
- [9] M. Penza, G. Cassano, Relative humidity sensing by PVA-coated dual resonator SAW oscillator, *Sens. Actuators B* 68 (2000) 300–306.
- [10] M. Neshkova, R. Petrova, V. Petrov, Piezoelectric quartz crystal humidity sensor using chemically modified nitrated polystyrene as water sorbing coating, *Anal. Chim. Acta* 332 (1996) 93–103.
- [11] F.P. Delannoy, B. Sorli, A. Boyer, Quartz crystal microbalance (QCM) used as humidity sensor, *Sens. Actuators A* 84 (2000) 285–291.
- [12] L.X. Sun, T. Okada, Simultaneous determination of the concentration of methanol and relative humidity based on a single Nafion(Ag)-coated quartz crystal microbalance, *Anal. Chim. Acta* 421 (2000) 83–92.
- [13] A.J. Cunningham, *Introduction to Bioanalytical Sensors*, Wiley, New York, 1998, pp. 307.
- [14] G. Sauerbrey, The use of quartz oscillators for weighing thin layers and for microweighing, *Z. Phys.* 155 (1959) 206–222.
- [15] S. Mintova, T. Bein, Nanosized zeolite films for vapor-sensing applications, *Microporous Mesoporous Mater.* 50 (2001) 159–166.
- [16] Y. Zhang, K. Yu, S. Ouyang, L. Luo, H. Hu, Q. Zhang, Z. Zhu, Detection of humidity based on quartz crystal microbalance coated with ZnO nanostructure films, *Physica B* 368 (2005) 94–99.
- [17] P.G. Su, Y.L. Sun, C.C. Lin, Novel low humidity sensor made of TiO<sub>2</sub> nanowires/poly(2-acrylamido-2-methylpropane sulfonate) composite material film combined with quartz crystal microbalance, *Talanta* 69 (2006) 946–951.
- [18] P.G. Su, Y.P. Chang, Low-humidity sensor based on a quartz-crystal microbalance coated with polypyrrole/Ag/TiO<sub>2</sub> nanoparticles composite thin films, *Sens. Actuators B* 129 (2008) 915–920.
- [19] M.E. Roberts, M.C. LeMieux, Z. Bao, Sorted and aligned single-walled carbon nanotube networks for transistor-based aqueous chemical sensors, *ACS Nano* 3 (2009) 3287–3293.
- [20] S.M. Lee, K.H. An, Y.H. Lee, G. Seifert, T. Frauenheim, A hydrogen storage mechanism in single-walled nanotubes, *J. Am. Chem. Soc.* 123 (2001) 5059–5063.
- [21] S. Iijima, Helical microtubes of graphitic carbon, *Nature* 354 (1991) 56–58.
- [22] J. Riu, A. Maroto, F.X. Rius, Nanosensors in environmental analysis, *Talanta* 69 (2006) 288–301.
- [23] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, *Science* 306 (2004) 666–669.

- [24] R.F. Service, Carbon sheets an atom thick give rise to graphene dreams, *Science* 324 (2009) 875–877.
- [25] Y.Y. Shao, J. Wang, H. Wu, J. Liu, I.A. Aksay, Y.H. Lin, Graphene based electrochemical sensors and biosensors: a review, *Electroanalysis* 22 (2010) 1027.
- [26] Y. Zhang, K. Yu, R. Xu, D. Jiang, L. Luo, Z. Zhu, Quartz crystal microbalance coated with carbon nanotube films used as humidity sensor, *Sens. Actuators A* 120 (2005) 142–146.
- [27] Y. Yao, X. Chen, H. Guo, Z. Wu, Graphene oxide thin film coated quartz crystal microbalance for humidity detection, *Appl. Surf. Sci.* 257 (2011) 7778–7782.
- [28] Q. Huang, D. Zeng, S. Tian, C. Xie, Synthesis of defect graphene and its application for room temperature humidity sensing, *Mater. Lett.* 83 (2012) 76–79.
- [29] L. Guo, H.B. Jiang, R.Q. Shao, Y.L. Zhang, S.Y. Xie, J.N. Wang, X.B. Li, F. Jiang, Q.D. Chen, T. Zhang, H.B. Sun, Two-beam-laser interference mediated reduction, patterning and nanostructuring of graphene oxide for the production of a flexible humidity sensing device, *Carbon* 50 (2012) 1667–1673.
- [30] P.G. Su, J.F. Tsai, Low-humidity sensing properties of carbon nanotubes measured by a quartz crystal microbalance, *Sens. Actuators B* 135 (2009) 506–511.
- [31] H.W. Chen, R.J. Wu, K.H. Chan, Y.L. Sun, P.G. Su, The application of CNT/Nafion composite material to low humidity sensing measurement, *Sens. Actuators B* 104 (2005) 80–84.
- [32] P.G. Su, Y.L. Sun, C.C. Lin, A low humidity sensor made of quartz microbalance coated with multi-walled carbon nanotubes/Nafion composite material films, *Sens. Actuators B* 115 (2006) 338–343.
- [33] J. Zhang, H.L. Zou, Q. Qing, Y.L. Yang, Q.W. Li, Z.F. Liu, X.Y. Qu, Z.L. Du, Effect of chemical oxidation on the structure of single-walled carbon nanotubes, *J. Phys. Chem. B* 107 (2003) 3712–3718.
- [34] H.L. Hsu, J.M. Jehng, Y. Sung, L.C. Wang, S.R. Yang, The synthesis, characterization of oxidized multi-walled carbon nanotubes, and application to surface acoustic wave quartz crystal gas sensor, *Mater. Chem. Phys.* 109 (2008) 148–155.
- [35] P.C.P. Watts, N. Mureau, Z. Tang, Y. Miyajima, J.D. Carey, S.R.P. Silva, The importance of oxygen-containing defects on carbon nanotubes for the detection of polar and non-polar vapors through hydrogen bond formation, *Nanotechnology* 18 (2007) 175701–175706.
- [36] J.A. Robinson, E.S. Snow, S.C. Bădescu, T.L. Reinecke, F.K. Perkins, Role of defects in single-walled carbon nanotube chemical sensors, *Nano Lett.* 6 (2006) 1747–1751.
- [37] Y. Okahata, M. Kawase, K. Niikura, F. Ohtake, H. Furusawa, Y. Ebara, Kinetic measurements of DNA hybridization on an oligonucleotide-immobilized 27-MHz quartz crystal microbalance, *Anal. Chem.* 70 (1998) 1288–1296.

## Biographies

**Pi-Guey Su** is currently a professor in Department of Chemistry at Chinese Culture University. He received his BS degree from Soochow University in Chemistry in 1993 and PhD degree in Chemistry from National Tsing Hua University in 1998. He worked as a researcher in Industrial Technology Research Institute, Taiwan, from 1998 to 2002. He joined as an Assistant Professor in the General Education Center, Chungchou Institute of Technology from 2003 to 2005. He worked as an Assistant Professor in Department of Chemistry at Chinese Culture University from 2005 to 2007. He worked as an Associate Professor in Department of Chemistry at Chinese Culture University from 2007 to 2010. His fields of interests are chemical sensors, gas and humidity sensing materials and humidity standard technology.

**Xian-Ren Kuo** received a BS degree in Chemistry from Chinese Culture University in 2013. He entered the MS course of chemistry at Chinese Culture University in 2013. His main areas of interest are humidity sensing materials.