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Low-humidity sensing properties of carbon nanotubes measured by a quartz crystal microbalance

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ABSTRACT

This study investigated the low-humidity sensing performance of raw multi-walled nanotubes (MWCNTs), oxidized MWCNTs (MWCNT-COOH) and Pd-modified MWCNT-COOH (Pd-MWCNT-COOH) thin films by using a quartz crystal microbalance (QCM). The characteristics of the thin films were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Water vapor molecules adsorbed onto the Pd-MWCNT-COOH thin film had a larger frequency shift than raw MWCNTs and MWCNT-COOH thin films. Adsorption dynamic analysis, molecular mechanics calculation (association constant), was applied to elucidate how surface modification and functionalization of MWCNTs increase the sensitivity to low-humidity.

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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, optic, field effect transistors (FETs), surface acoustic wave (SAW) and quartz crystal microbalance (QCM), 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 change [2]. Sauerbrey [3] first derived the quantitative relationship between changes in frequency Δf (Hz) of the piezoelectric crystal and mass changes caused by mass loading on the piezoelectric crystal surface as follows:

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

where f_0 (MHz) denotes the basic frequency of the unloaded piezoelectric crystal, A (cm^2) represents the surface area of the electrode, and Δm (g) is the change in mass on the crystal surface.

Carbon nanotubes (CNTs) have attracted considerable interest for demanding applications in the field of gas sensing due to their unique structure and properties [4,5]. Both single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) are extremely promising due to their high surface areas provided by their central hollow cores and outside walls for gas adsorption, as well as their tendency to change electrical properties at room temperature in the presence of different gases at low concentrations [6–11]. These CNTs may be a promising solution for detecting low levels of humidity.

Notably, CNTs prepared as films coated on a QCM electrode have been reported to detect humidity [12]. The performance characteristics of QCM-based sensors primarily depend on the chemical nature and physical properties of the coating materials. The MWCNTs were treated by ball milling and the hydrogen plasma technique and then coated on a QCM as a relative humidity sensor [12]. Recently, CNTs-based nanocomposite materials were prepared as films coated on an electrode of QCM to detect low-humidity in our previous studies [13–16]. These materials included single-walled carbon nanotube/Nafion composite material (SWCNTs/Nafion) [13,14], multi-walled carbon nanotube/Nafion composite material (MWCNTs/Nafion) [14], TiO_2 nanowires/poly(2-acrylamido-2-methylpropane) sulfonate (TiO_2 NWs/PAMPS) [15]

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Table 1
The sensing characteristics (sensitivity and linearity) of the prepared devices in our previous works [13–16].

Sensing materials	Sensing curve	
	Slope($-\Delta\text{Hz}/\Delta\text{ppm}_v$) ^a	Correlation coefficient (R^2) ^b
SWCNTs/Nafion	0.0894	0.9901
MSWCNTs/Nafion	0.1942	0.9427
TiO ₂ NWs/PAMPS	0.2610	0.9738
PPy/Ag/TiO ₂ NPs	0.0128	0.9988

^a The slope was defined as the slope value of linear fitting curve at humidity working range from 23 to 1594 ppm_v.

^b The correlation coefficient (R^2) was defined as the R^2 -value of linear fitting curve at humidity working range from 23 to 1594 ppm_v.

and polypyrrole/TiO₂ nanoparticles (PPy/TiO₂ NPs) [16]. The low-humidity sensing properties, based on the sensitivity and the linearity, of the prepared devices are shown in Table 1. However, the QCM-based low-humidity sensor based on CNTs has not been studied sufficiently. In this study, raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH were used to construct QCM-based low-humidity sensors. This study investigates how the microstructures of CNTs and low-humidity sensing properties are related. Furthermore, the adsorption dynamics of water vapor molecules onto raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films coated on the QCM and the CNT microstructure 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 [17] of raw chemical vapor deposition (CVD) grown MWCNTs (200 mg, Sunnano Inc.) using an H₂SO₄/HNO₃ 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. The Pd-MWCNT-COOH dispersion was prepared using a photocatalytic reaction [18]. The prepared MWCNT-COOH dispersion was placed in the acidic solution of PdCl₂ at a proper molar ratio of 0.01; the Pd-MWCNT-COOH was then formed by photoreduction under UV light (Spectroline, 11SC-1, 254 nm) for 30 min. The residue was subsequently repeatedly washed with deionized water.

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 and Pd-MWCNT-COOH thin films had mass values 0.037, 0.044 and 0.068 μg, respectively, on the QCM disk. Unless otherwise stated, all measurements were taken at room temperature, around 23.0 ± 1.5 °C.

2.2. Instruments and analysis

A divided humidity generator was the main device for generating the testing gases. The required water vapor concentration

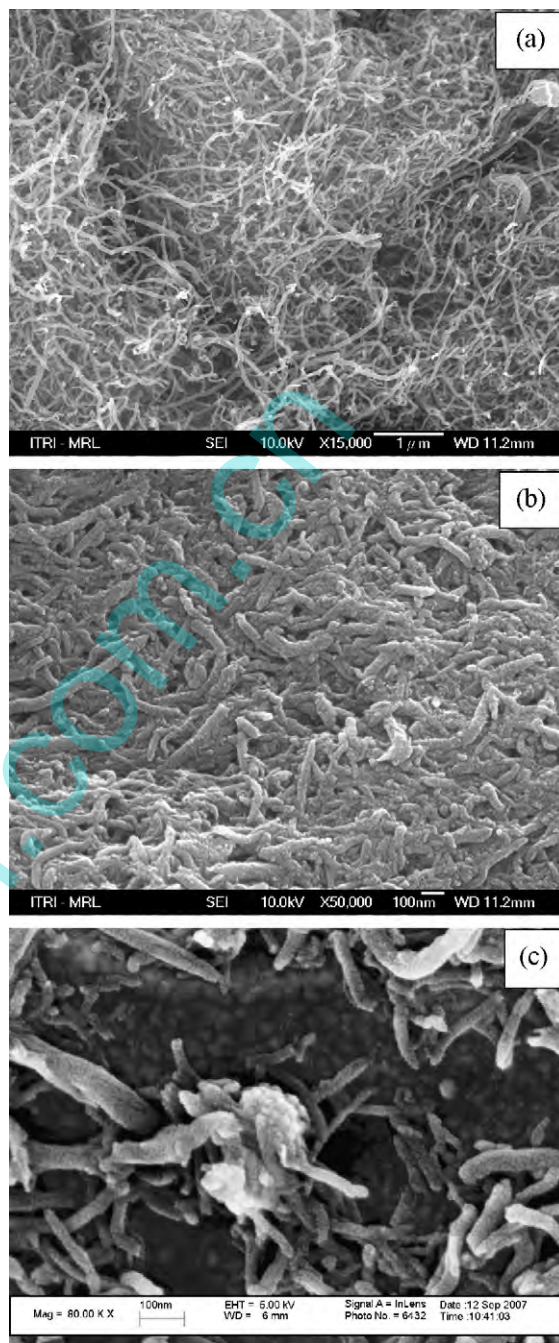


Fig. 1. FE-SEM micrographs of (a) raw MWCNTs, (b) MWCNT-COOH and (c) Pd-MWCNT-COOH thin films.

was generated by adjusting the proportions of dry and humid air that were generated by the divided flow humidity generator. The dryness of the gas limited the lowest testing point. A low-humidity hygrometer (HYGROCLIP IC-3, Rotronic Inc.) and a QCM sensor were connected to an outlet of the divided flow humidity generator, and the low-humidity hygrometer was used as the reference standard to calibrate the QCM sensor, as described elsewhere [14,15]. The volume ratio of the moist air was adjusted according to the reading of the low-humidity hygrometer calibrating to the CMS/NML (Center for Measurement Standards/National Measurement Laboratory) humidity laboratory. The volume ratio of the moist air was calculated by the following

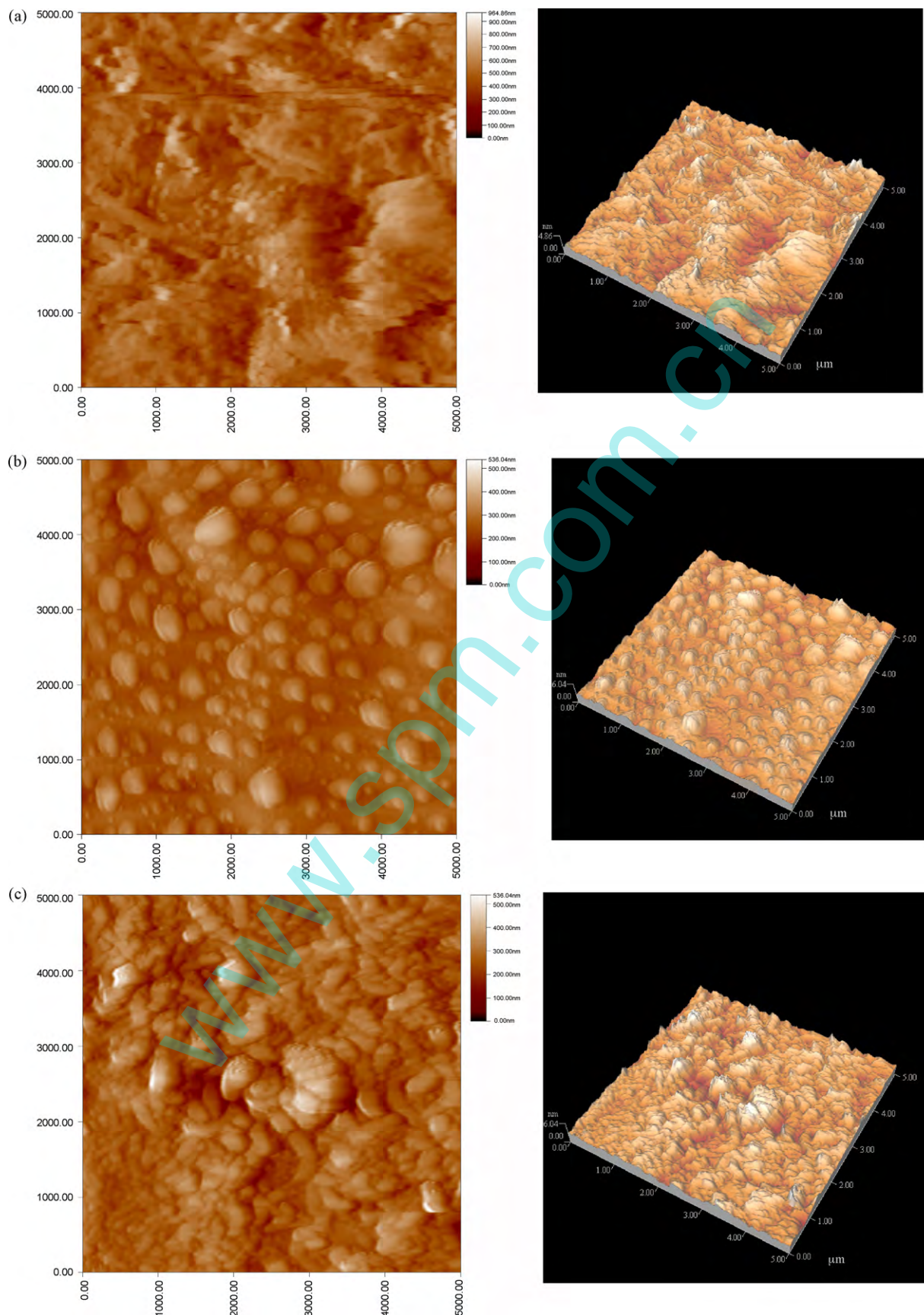


Fig. 2. AFM micrographs (5 μm × 5 μm) of (a) raw MWCNTs, (b) MWCNT-COOH and (c) Pd-MWCNT-COOH thin films.

equation:

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

$$\text{ppm}_v = \frac{e}{p - e} \times 10^6 \text{ (ideal gas)} \quad (3)$$

where V_v is the volume of water vapor, V is the total volume, e is the partial pressure of water vapor and P is the total pressure. Measurement procedures were recorded as follows. Firstly the synthetic dry air was passed through the detection chamber until the frequency of QCM became stable; then the water vapor at the required concentration was flowed into the detection chamber; finally, the synthetic dry air was passed through the detection chamber until the frequency of QCM had returned to its initial value. The initial volume ratio of the moist air was 2.77 ppm_v for all experiments.

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 (FE-SEM, JEOL, JSM 6335F) and an atomic force microscope (AFM, Ben-Yuan, CSPM 4000) in tapping mode.

3. Results and discussion

3.1. Surface microstructure characteristics of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films

Fig. 1 presents the SEM images of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films. Fig. 1(a) presents the diameter of the raw MWCNTs, in the 30–45 nm range, used in this study. The surface of MWCNTs was smooth. Many small and irregular pores were observed due to their random entanglement and alignment in nanotubes. Fig. 1(b) shows the surface microstructure of the MWCNT-COOH mat coated on the QCM. The surface of the MWCNTs became rough and their length was shorter than that of raw MWCNTs. Fig. 1(c) presents the surface microstructure of the Pd-MWCNT-COOH mat coated on the QCM. The Pd nanolumps gathered together and covered the sidewall of the MWCNTs.

The surface morphology and uniformity of CNT thin films were investigated by AFM. Fig. 2(a)–(c) shows the surface topography of 5 μm × 5 μm raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films, respectively, coated on the QCM. The data of the root mean square (RMS) roughness of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films was 73.4, 36.5 and 47.5 nm, respectively. Fig. 2(a) shows large amounts of raw MWCNTs randomly organized on the QCM. Fig. 2(b) shows large amounts of granules on the QCM. The difference in surface morphologies between MWCNT-COOH and Pd-MWCNT-COOH thin films was due to formation of Pd nanolumps on the surface of MWCNT-COOH (Fig. 2(b) and (c)). These experimental results indicate that the surface properties of CNTs have an important role in low-humidity sensing.

3.2. Low-humidity sensing properties of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films

Fig. 3 plots the frequency shifts of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films as a function of time for various volume ratios of moist air in the range of 2798–8964 ppm_v. Table 2 lists the corresponding sensitivities. Fig. 4 plots calibration curve results for raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films. When the volume ratio of moist air was 2798 ppm_v, the sensitivity of raw MWCNT, MWCNT-COOH and Pd-MWCNT-COOH thin films was 0.0071, 0.0248 and 0.0375, respectively (Table 2), demonstrating that the response of the Pd-MWCNT-COOH film

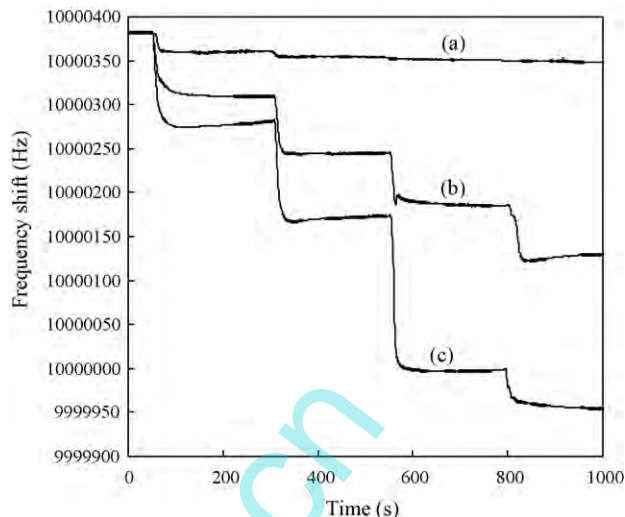


Fig. 3. Frequency shifts (Hz) as a function of time (s) for different volume ratio of the moist air on (a) raw MWCNTs, (b) MWCNT-COOH and (c) Pd-MWCNT-COOH thin films.

Table 2

Sensitivity to humidity of CNTs thin films coated on QCM for different volume ratios of moist air.

Δppm_v^b	Sensitivity ^a		
	Raw MWCNTs	MWCNT-COOH	Pd-MWCNT-COOH
2798	0.0071	0.0248	0.0375
5568	0.0050	0.0241	0.0378
7542	0.0040	0.0255	0.0504
8963	0.0037	0.0283	0.0468

^a The sensitivity of the various sensing films was defined as $-\Delta \text{Hz}/\Delta \text{ppm}_v$ [29].

^b The Δppm_v was defined as the volume ratio subtracted by the initial volume ratio of moisture air (2.77 ppm_v).

was higher than those of the raw MWCNTs and MWCNT-COOH thin films, especially at low levels of humidity. The calibration curve of the Pd-MWCNT-COOH film had an acceptable linear behavior with a slope and a correlation relationship coefficient of 0.0541 Hz/ppm_v and 0.9663, respectively. Table 3 shows the comparison results of low-humidity sensing characteristics of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films.

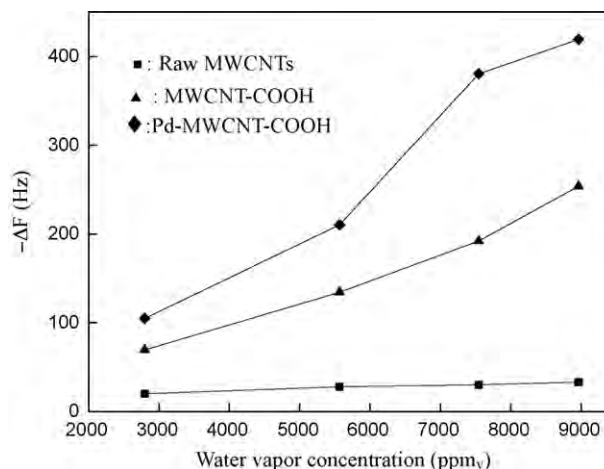


Fig. 4. Frequency change ($-\Delta F$) as a function of volume ratio (ppm_v) for raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films.

Table 3

The linear sensing characteristics of CNTs thin films coated on QCM.

	Sensing characteristics	
	Slope	Linearity ^a
Raw MWCNTs	0.0021	0.9726
MWCNT-COOH	0.0293	0.9821
Pd-MWCNT-COOH	0.0541	0.9663

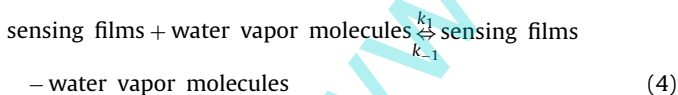
^a The linearity was defined as the R^2 -value of linear fitting curve in the humidity range from 2798 to 8964 ppm_v.

The raw MWCNTs formed a porous structure (Figs. 1(a) and 2(a)). However, CNTs are known to be highly hydrophobic; therefore, the water-tube interaction is weak. Moreover, few water vapor molecules accumulated around these pores; consequently, inducing capillary condensation at a low-humidity is difficult [19]. When raw MWCNTs were treated with acid, the presence of COOH groups' sites on the MWCNTs has been verified [17,20]. The defective sites (COOH) form low-energy adsorption sites that also serve as nucleation sites for analyte condensation. Therefore, the MWCNT-COOH thin film had higher sensitivity to humidity than raw MWCNTs, 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 [21,22]. When MWCNT-COOH was functionalized with Pd (Figs. 1(c) and 2(c)), Pd formed metallic granules on the surface of MWCNT-COOH, the number of adsorption sites increased, presenting a high local charge density and a strong electrostatic field, and thereby improved the sensitivity of Pd-MWCNT-COOH than that of the MWCNT-COOH thin film. Furthermore, water vapor molecules were associatively adsorbed on the Pd surface and dissociatively adsorbed as OH or OH/H₂O complexes with the assistance of pre-adsorbed O atoms on the Pd surface [23–26].

3.3. Adsorption properties of raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films

The adsorption behaviors of water vapor molecules by raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films were compared. The following reaction [27,28] explained the increase in sensitivity to low-humidity of the raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films.

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



where k_1 and k_{-1} are adsorption and desorption rate constant, respectively. The amount of water vapor molecules, Δm_t , formed on the sensing films at time t , is then given by the following equations under Langmuir isotherm adsorption conditions [27,28]:

$$\begin{aligned} \Delta m_t &= [\text{sensing films} - \text{water vapor molecules}]_t \\ &= \Delta m_\infty \left[1 - \exp\left(\frac{-t}{\tau}\right) \right] \end{aligned} \quad (5)$$

$$\tau^{-1} = k_1[\text{water vapour molecules}] + k_{-1} \quad (6)$$

where Δm_∞ denotes the maximal amount of water vapor molecules adsorbed on the sensing films at $t \rightarrow \infty$ and τ is relaxation time. Adsorption time courses at different concentrations (0.0534–0.2356 M) were derived using Eqs. (5) and (6). Fig. 5 plots the linear correlation between reciprocal relaxation time (τ^{-1}) of adsorption and the concentration of water vapor on sensing films

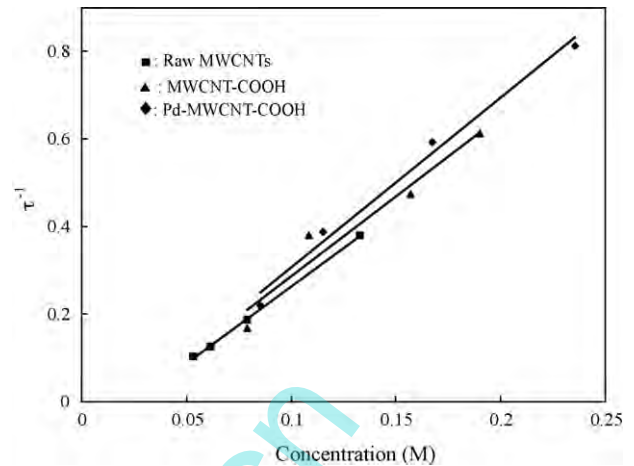


Fig. 5. Linear plot of the reciprocal of relaxation time (τ^{-1}) against vapor concentration (M) for raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH thin films.

Table 4

Kinetic parameters for adsorption and desorption of water vapor molecules onto CNTs thin films.

Films	Adsorption rate constant, k_1 ($M^{-1} s^{-1}$)	Desorption rate constant, k_{-1} (s^{-1})	Association constant, K (M^{-1})
Raw MWCNTs	3.528	0.089	39.46
MWCNT-COOH	3.662	0.080	45.94
Pd-MWCNT-COOH	3.883	0.082	47.30

(raw MWCNTs, MWCNT-COOH and Pd-MWCNT-COOH). Fig. 5 and Eq. (6) 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 4). The Pd-MWCNT-COOH-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 Pd-MWCNT-COOH than on raw MWCNTs and MWCNT-COOH films. The association constant K of water vapor molecules onto the sensing films was in the following order: Pd-MWCNT-COOH > MWCNT-COOH > raw MWCNTs. Therefore, the larger association constant ($K=47.30 M^{-1}$) of water vapor onto the Pd-MWCNT-COOH film than onto the raw MWCNTs and MWCNT-COOH films 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 surface of CNTs-based materials plays a predominant role at low-humidity. Therefore, the Pd-MWCNT-COOH thin film was more sensitive to water vapor molecules than raw MWCNTs and MWCNT-COOH thin films (Table 2).

4. Conclusion

The surface modification and functionalization of MWCNTs can enhance the surface properties of MWCNTs and increase the sensitivity of MWCNTs to low levels of humidity.

The Pd-MWCNT-COOH coated on the QCM electrode had high sensitivity (especially at low-humidity levels) and acceptable linearity. The Pd-MWCNT-COOH thin film combined with QCM is reliable technique for measuring trace humidity.

Based on the Langmuir isotherm adsorption assumption, the adsorption rate constant k_1 for water vapor molecules on Pd-MWCNT-COOH is larger than those for the raw MWCNTs and MWCNT-COOH coated on QCM. Moreover, molecular mechanics

calculations supported the experimental results, indicating that the high sensitivity of the Pd–MWCNT–COOH thin film to water vapor molecules is ascribed to the slightly larger association constant *K* of the Pd–MWCNT–COOH thin film to water vapor molecules than those of raw MWCNTs and MWCNT–COOH thin films due to the COOH groups sites and Pd metallic granules formed on the surface of MWCNTs.

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References

- [1] P.R. Story, D.W. Galipeau, R.D. Mileham, A study of low-cost sensors for measuring low relative humidity, *Sens. Actuator B* 24–25 (1995) 681–685.
- [2] A.J. Cunningham, *Introduction to Bioanalytical Sensors*, Wiley, New York, 1998, p. 307.
- [3] G. Sauerbrey, The use of quartz oscillators for weighing thin layers and for microweighing, *Z. Phys.* 155 (1959) 206–222.
- [4] S. Iijima, Helical microtubes of graphitic carbon, *Nature* 354 (1991) 56–58.
- [5] J. Riu, A. Maroto, F.X. Rius, Nanosensors in environmental analysis, *Talanta* 69 (2006) 288–301.
- [6] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Nanotube molecular wires as chemical sensors, *Science* 287 (2000) 622–625.
- [7] A. Flujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, S. Suzuki, Y. Achiba, Gas adsorption in the inside and outside of single-walled carbon nanotubes, *Chem. Phys. Lett.* 336 (2001) 205–211.
- [8] G.U. Sumanasekera, C.K.W. Adu, F. Fang, P.C. Eklund, Effect of gas adsorption on electrical transport in single-walled carbon nanotubes, *Phys. Rev. Lett.* 85 (2000) 1096–1099.
- [9] A. Zahab, L. Spina, P. Poncharal, Water-vapor effect on the electrical conductivity of a single walled carbon nanotubes, *Phys. Rev. B* 62 (2000) 10000–10003.
- [10] O.K. Varghese, P.D. Kichambre, D. Gong, K.G. Ong, E.C. Dickey, C.A. Grimes, Gas sensing characteristics of multi-walled carbon nanotubes, *Sens. Actuator B* 81 (2001) 32–41.
- [11] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng, K.J. Cho, Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection, *Nano Lett.* 3 (2003) 347–351.
- [12] 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. Actuator B* 120 (2005) 142–146.
- [13] 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. Actuator B* 104 (2005) 80–84.
- [14] 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. Actuator B* 115 (2006) 338–343.
- [15] P.G. Su, Y.L. Sun, C.C. Lin, Novel low humidity sensor made of TiO₂ nanowires/poly(2-acrylamido-2-methylpropane sulfonate) composite material film combined with quartz crystal microbalance, *Talanta* 69 (2006) 946–951.

- [16] P.G. Su, Y.P. Chang, Low-humidity sensor based on a quartz-crystal microbalance coated with polypyrrole/Ag/TiO₂ nanoparticles composite thin films, *Sens. Actuator B* 129 (2008) 915–920.
- [17] J. Zhang, H.L. Zou, Q. Qing, Y.L. Yang, Q.W. Li, Z.F. Liu, X.Y. Quo, Z.L. Du, Effect of chemical oxidation on the structure of single-walled carbon nanotubes, *J. Phys. Chem. B* 107 (2003) 3712–3718.
- [18] H. Yoshiki, H. Kitahara, K. Hashimoto, A. Fujishima, Pattern formation of Cu layer by photocatalytic reaction of ZnO thin film, *J. Electrochem. Soc.* 142 (1995) L235–L237.
- [19] J.T.W. Yeow, J.P.M. She, Carbon nanotube-enhanced capillary condensation for a capacitive humidity sensor, *Nanotechnology* 17 (2006) 5441–5448.
- [20] 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.
- [21] 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.
- [22] 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.
- [23] C. Nyberg, C.G. Tengstal, Adsorption and reaction of water, oxygen and hydrogen on Pd (1 0 0): identification of adsorbed hydroxyl and implications for the catalytic H₂–O₂ reaction, *J. Chem. Phys.* 80 (1984) 3463–3468.
- [24] C. Nyberg, P. Uvdal, The oxygen–water reaction on Pd(1 0 0): observation of a precursor complex, *J. Chem. Phys.* 84 (1986) 4631–4635.
- [25] C. Clay, L. Cummings, A. Hodgson, Mixed water/OH structures on Pd(1 1 1), *Surf. Sci.* 601 (2007) 562–568.
- [26] Z. Zhao, M. Knight, S. Kumar, E.T. Eisenbraun, M.A. Carpenter, Humidity effects on Pd/Au-based all-optical hydrogen sensors, *Sens. Actuator B* 129 (2008) 726–733.
- [27] 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.
- [28] 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.
- [29] 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.

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