



Humidity sensing properties of calix[4]arene and functionalized calix[4]arene measured using a quartz-crystal microbalance

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ABSTRACT

Humidity sensors were made by coating 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (TBHC) and 5-(4'-nitrophenyl)azo-25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (NTBHC) thin films on a gold electrode of a quartz crystal microbalance (QCM). The thin films were analyzed by atomic force microscopy (AFM). The humidity sensing properties, including sensitivity, sensing linearity, hysteresis, cross-sensitivity effects and long-term stability were also investigated. Water vapor molecules that were adsorbed onto the NTBHC thin film exhibited a larger frequency shift than those adsorbed onto TBHC thin films. Adsorption dynamic analysis and a molecular mechanical calculation (of the association constant) were made to elucidate the way in which a substituent on the upper and lower rims of calix[4]arene increases the sensitivity to humidity.

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1. Introduction

Humidity sensors are widely used in many fields such as improving quality of life and enhancing industrial processes. The investigation of a good humidity sensor is focused on the improvement of many requirements, including linear response, high sensitivity, fast response time, chemical and physical stability, a wide operating range of humidity, and low cost. 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 changes [1]. Sauerbrey [2] first derived the quantitative relationship between changes in frequency Δf (Hz) of the piezoelectric crystal and mass change 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 (cm²) represents the surface area of the electrode, and Δm (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.

Calixarenes are macrocyclic molecules that are formed by the condensation of phenols with formaldehydes. These compounds with various cavity shapes and sizes form host–guest complexes. The calixarene molecules act as a host and many charged or uncharged species act as guests. The sensitivity and selectivity of calixarenes vary with the numbers of aryl fragments and the binding of various functional groups to upper and lower rims. This fact has resulted in their use in the separation of organic compounds, liquid membranes, biosensors and chemical sensors [3–11]. Hartmann et al. [8] and Koshets et al. [9] fabricated calixarene film-coated QCM sensors for detecting volatile organic compounds (VOCs). Filenko et al. [10] fabricated discontinuous gold films (DGF)-based sensors that were coated with calixarenes for detecting methanol vapors. Richardson et al. [11] fabricated an optical NO₂ gas sensor that was based on a mixed-layered film of calix[8]arene/porphyrin. However, most calixarenes have hydrophobic properties and so are not employed as practical humidity sensors.

To improve the hydrophilic properties of calixarenes, water-soluble calix[n]arene derivatives have been synthesized, and carboxylates, phosphates, ammonium or sulphonated functional groups have been introduced either at the upper rim or at the lower rim of the parent calixarenes [4,12]. Recently, Okur et al. [13] fabricated humidity sensors that were made of calix[4]arene derivatives with both carboxylate and sulphonate groups that were coated on QCM. However, they exhibit the intrinsic shortcomings of instability at high humidity and large hysteresis. Liu

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et al. [14], fabricated chromogenic amine sensors that were based on nitrophenylazo-calix[4]arenes film. However, no attempt has been made to produce a humidity sensor that is based on a thin film consists of functionalized calix[4]arene with benzoyloxy and nitrophenylazo groups that is coated on QCM. Accordingly, in this work, two functionalized calix[4]arenes, 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (TBHC) and 5-(4'-nitrophenyl)azo-25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (NTBHC), were synthesized and coated on QCM to form humidity sensors. The thickness and surface roughness of the thin films were analyzed using scanning electron microscopy (SEM) and tapping mode atomic force microscopy (AFM), respectively. This study investigates how the substituent on the upper and lower rims of calix[4]arene is related to the humidity sensing properties, and it places special emphasis is laid on the most important properties of sensitivity and linearity. Their humidity-sensing properties, including hysteresis, cross-sensitivity effects, and long-term stability were studied. Furthermore, the dynamics of adsorption of water vapor molecules onto TBHC and NTBHC thin films that are coated on the QCM are used to elucidate the humidity sensing properties (sensitivity).

2. Experimental

2.1. Humidity sensor fabrication

2.1.1. Materials

The synthesis of the 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (TBHC) and 5-(4'-nitrophenyl)azo-25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (NTBHC) have been described in previous work [15]. The TBHC was prepared by "lower rim" benzylation of calix[4]arene with benzoyl chloride in an ice bath for 1 h. Recrystallization from CHCl_3 and CH_3OH afforded the TBHC as colorless thin plate-like crystals. The NTBHC was prepared from the TBHC in two-step process to introduce the upper *p*-nitrophenylazo moiety. Structure and purity of all these compounds were verified by NMR and MS. The chemical structures of these calix[4]arenes were shown in Fig. 1.

2.1.1.1. 25,26,27-Tribenzoyloxy-28-hydroxy-calix[4]arene (TBHC). Yield 81%; mp: 268–270 °C; ^1H NMR (CDCl_3) δ 6.52–8.10 (m, 27H), 5.44 (s, 4H), 3.83–3.90 (d, 2H), 3.75–3.82 (d, 2H), 3.63–3.71 (d, 2H), 3.43–3.50 (d, 2H); ^{13}C NMR δ 165.0, 164.4, 153.3, 148.8, 147.2, 134.3, 134.0, 133.7, 133.4, 133.1, 131.8, 131.3, 130.8, 130.0, 129.7, 129.3, 129.2, 128.6, 128.3, 128.2, 126.5, 125.6, 120.2, 37.9, 32.9; FAB-MS m/e 737 ($\text{M}^+ + 1$).

2.1.1.2. 5-(4'-Nitrophenyl)azo-25,26,27-tribenzoyloxy-28-hydroxy-calix[4]arene (NTBHC). Yield 33%; mp: 290–291 °C; ^1H -NMR (CDCl_3) δ 8.35–8.36 (d, 2H), 7.84–7.86 (d, 2H), 7.48 (s, 2H), 7.27–7.99 (m, 15H), 6.61–7.08 (m, 9H), 5.96 (s, 1H), 3.93–3.91 (d, 2H), 3.79–3.76 (d, 2H), 3.70–3.67 (d, 2H), 3.67–3.64 (d, 2H); ^{13}C NMR δ 164.3, 163.9, 157.2, 155.8, 148.3, 148.2, 147.0, 145.7, 133.8, 133.7, 133.4, 133.3, 131.8, 131.4, 131.0, 130.9, 130.8, 129.5, 128.7, 128.6, 128.5, 127.8, 126.2, 125.2, 124.7, 123.1, 37.3, 33.1; FAB-MS m/e 886 ($\text{M}^+ + 1$).

2.1.2. Fabrication of the QCM electrodes

The AT-cut quartz crystals with a fundamental resonance frequency of 10 MHz and a frequency counter were obtained from ANT Technologies Corp., Taiwan. The surface area of the gold electrode on a QCM was 0.102 cm^2 . 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 chloroform solutions of these calix[4]arenes by dip-coating, followed by heating at 60 °C for 15 min in air. Consequently, TBHC and

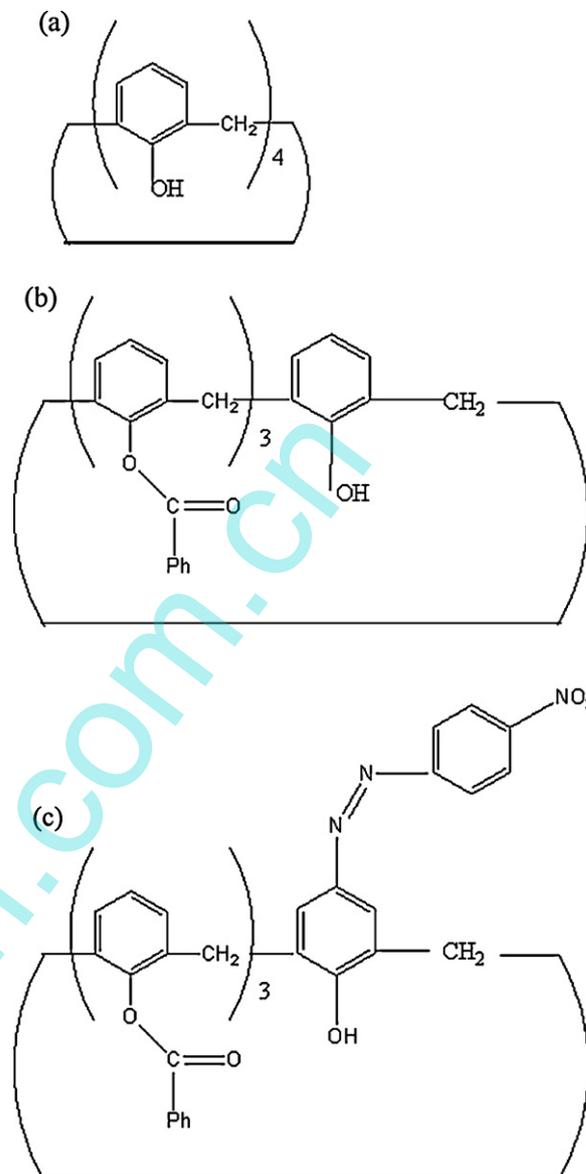


Fig. 1. Chemical structures of (a) calix[4]arene; (b) TBHC and (c) NTBHC.

NTBHC thin films had mass values 1.73 and 1.22 μg , respectively, on the QCM disk.

2.2. Instruments and analysis

As shown in Fig. 2, 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 controllers (Hastings) and flow display power-supply used is the Protec PC-540 manufactured by Sierra Instruments Inc., as described elsewhere [16]. The RH values were measured using a calibrated 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 RH values and temperature would be adjusted according to the reading of the humidity

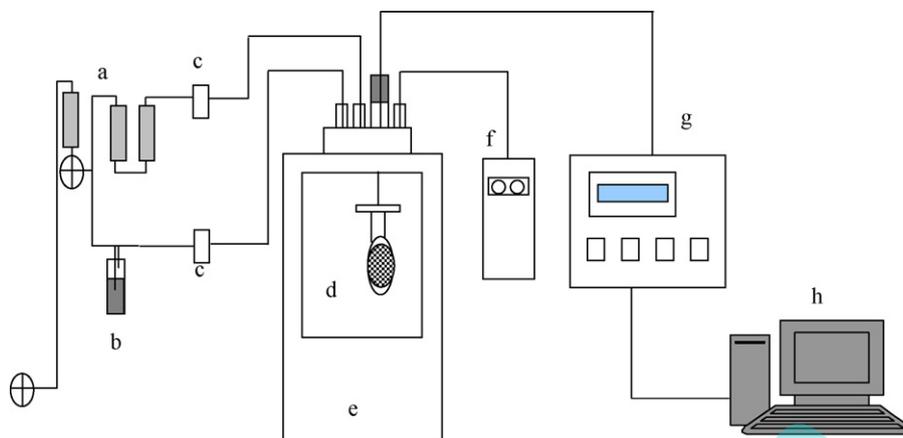


Fig. 2. Schematic diagram of experimental set-up for the QCM sensor measurement and low humidity atmosphere controller. (a) Molecular sieve and desiccating agent; (b) water; (c) mass flow controller; (d) detecting chamber and QCM; (e) thermostat; (f) humidity hygrometer; (g) oscillator and frequency counter and (h) PC.

hygrometer calibrated at the CMS/NML (Center for Measurement Standards/National Measurement Laboratory) humidity laboratory. 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 RH values 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. All the measurements were performed at the room temperature $23.0 \pm 1.5^\circ\text{C}$ and controlled by the thermostat. The surface microstructure of the thin film that was coated on a 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 thickness of the thin film was investigated using a field emission scanning electron microscope (FE-SEM, JEOL, JSM 6335F).

3. Results and discussion

3.1. Characteristics of surface microstructures of TBHC and NTBHC thin films

The surface morphology of calix[4]arene derivatives thin films were investigated by AFM. Fig. 3(a) and (b) show the surface

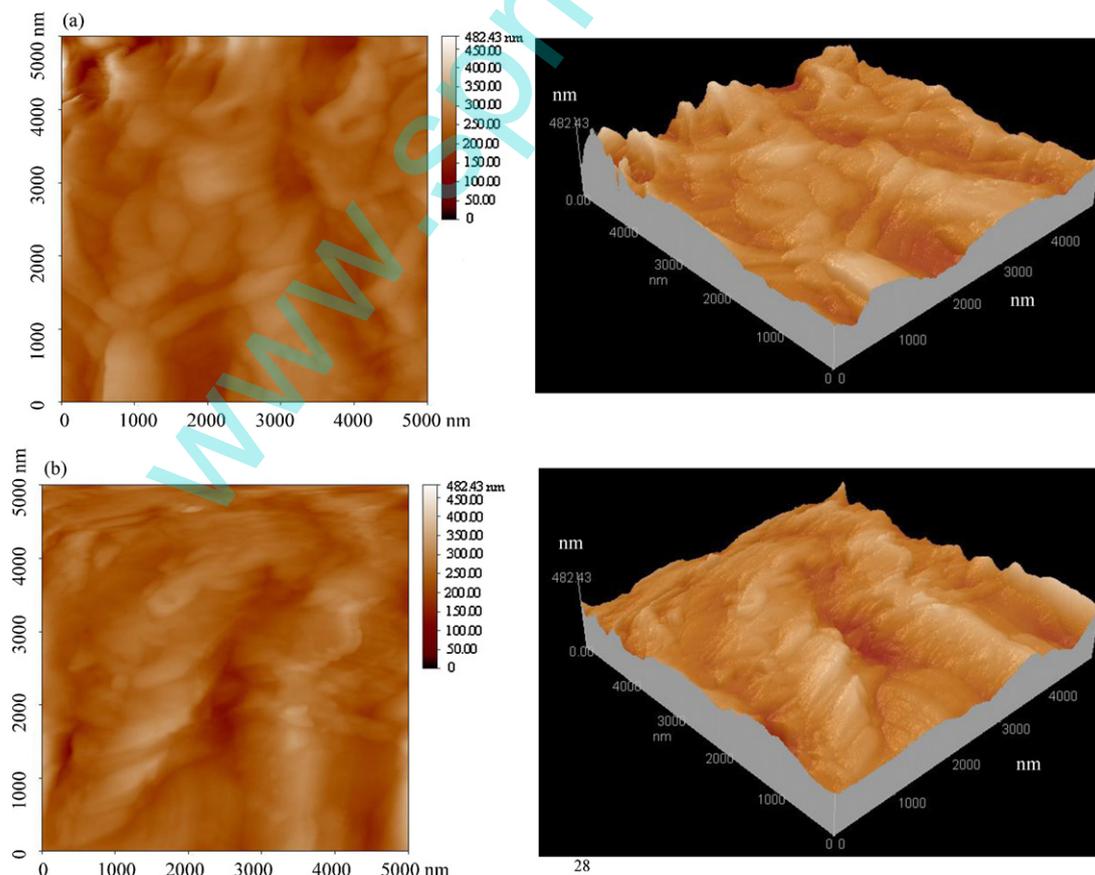


Fig. 3. AFM images of (a) TBHC and (b) NTBHC thin films.

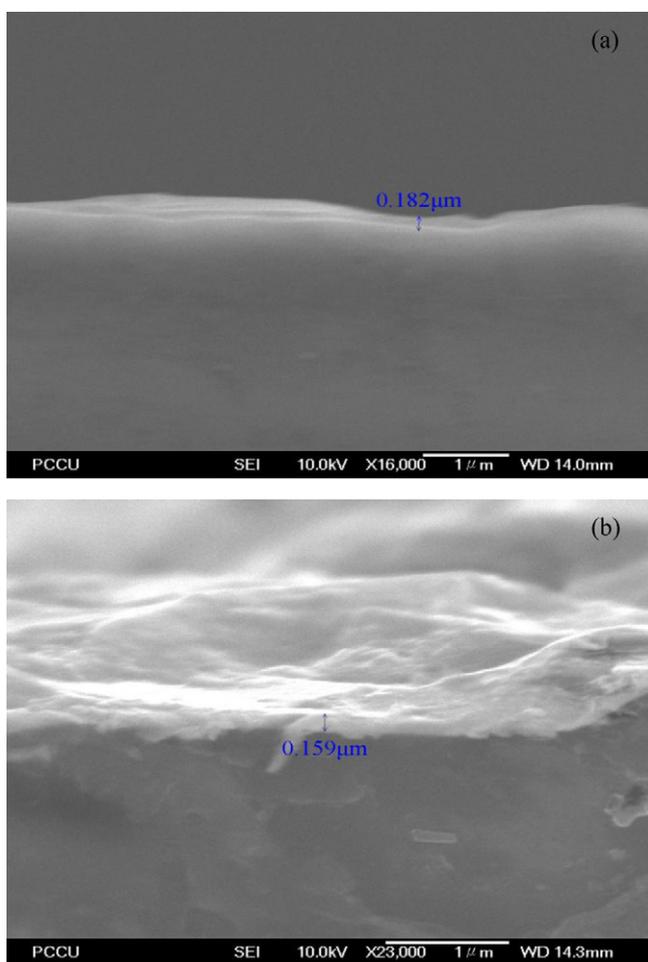


Fig. 4. FE-SEM micrographs of cross sectional view of (a) TBHC and (b) NTBHC thin films on QCM chip surface.

topography of $5 \mu\text{m} \times 5 \mu\text{m}$ TBHC and NTBHC thin films, respectively, coated on the QCM. The data of the root mean square (RMS) roughness of TBHC and NTBHC thin films was 33.3 and 32.8 nm, respectively. Both TBHC and NTBHC thin films had a smooth surface and their not values of roughness did not differ significantly. Fig. 4 presents a cross-sectional view of the TBHC and NTBHC thin films on a QCM chip. The thicknesses of the TBHC and NTBHC thin films were calculated to be 182 and 159 nm, respectively.

3.2. Humidity sensing properties of calix[4]arene, TBHC and NTBHC thin films

Fig. 5 plots the frequencies of calix[4]arene, TBHC and NTBHC thin films as a function of time at various RH values. Fig. 6 plots the calibration curves of TBHC and NTBHC thin films. Table 1 shows the results of sensitivity (defined as the slope of frequency change ($-\Delta\text{Hz}$) versus RH) and linearity (a correlation coefficient that is defined as the R -squared value of the linear fitting curve in the range from 20% to 90% RH). The calix[4]arene thin film (Fig. 5(a)) exhibited only a small change in frequency from 20% to 90% RH, undoubtedly owing to its hydrophobic property. The TBHC and NTBHC thin films (Fig. 5(b) and (c)), exhibited a changing frequencies from 20% to 90% RH. From 20% to 70% RH, the sensitivity (slope) of the TBHC and NTBHC thin films to humidity were 3.776 and 5.140, respectively (Table 1), demonstrating that the response of the NTBHC thin film to humidity was stronger than that of the TBHC thin film, especially at low RH. The TBHC thin film exhibited a steeply increasing frequency with RH above 70% RH (Fig. 5(b) and Fig. 6). Therefore, the linearity

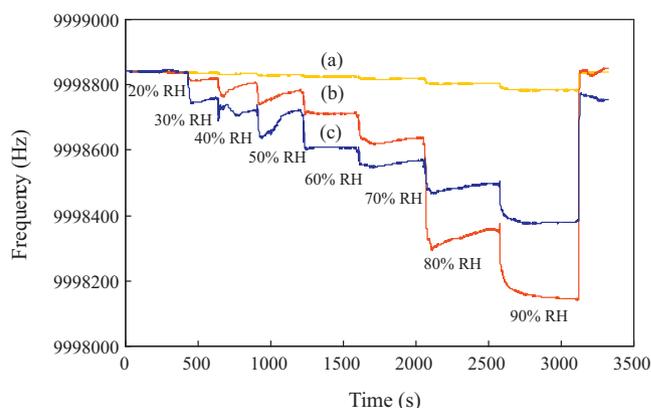


Fig. 5. Frequency shifts (Hz) as a function of time (s) at various RH values on (a) calix[4]arene; (b) TBHC and (c) NTBHC thin films.

of NTBHC thin film was better than that of the TBHC thin film over a wide range of humidities, 20–90% RH (Table 1).

AFM analysis (Fig. 3) reveals that the surface morphologies of the TBHC and NTBHC thin films differed very little. Therefore, the fact that the sensitivity of the NTBHC thin film exceeded that of the TBHC thin film was not related to their surface properties. Calix[4]arenes in the cone conformation nicely accommodated a circular array, in which all of the $-\text{OH}$ groups were in the same plane, since the cone conformation was homoplanar and the intramolecular hydrogen bond strengths were maximized. This fact suggests that the $-\text{OH}$ groups are protected by being buried in the cavities of the molecules. It may explain why the calix[4]arenes were highly hydrophobic, and why, therefore, the water–calix[4]arene interaction was weak. When calix[4]arene was substituted by benzoyloxy groups on the lower rim (of the TBHC thin film) the conformational mobility was increased, yielding an inverse cone conformation by steric hindrance, causing the $-\text{OH}$ groups to be easily projected outside the cavity [17]. The sites ($-\text{OH}$) were low-energy adsorption sites for the condensation of water vapor. Therefore, the TBHC thin film was more sensitive to humidity than was calix[4]arene, because water vapor was preferentially adsorbed on $-\text{OH}$ by the formation of hydrogen (H) bonds. When TBHC was further substituted with nitrophenylazo groups on the upper rim to form NTBHC, the number of adsorption sites increased, producing strong local polarity, and thereby improving the sensitivity of the NTBHC thin film above that of the TBHC thin film. The humidity sensor that was made of NTBHC thin film was further tested to evaluate its hysteresis, cross-sensitivity effects and long-term stability.

Hysteresis is the time lag between the adsorption and desorption processes, and is typically used to estimate the reliability of humidity sensors [18]. Fig. 7 plots the hysteresis of the humidity

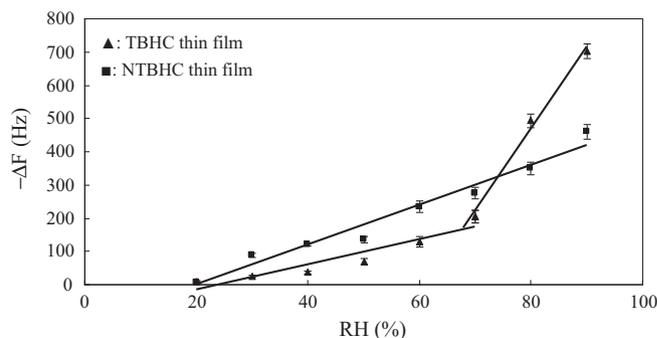
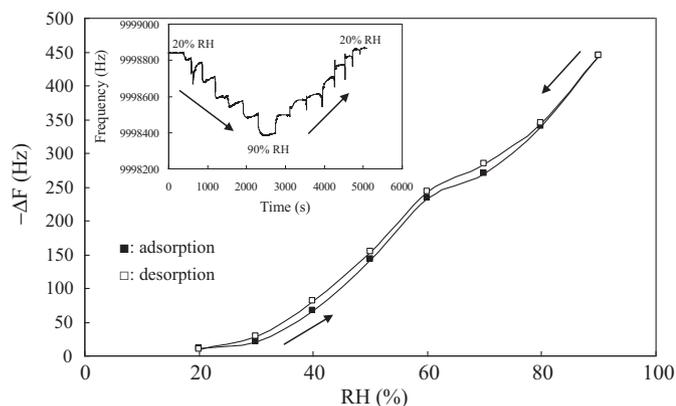


Fig. 6. Frequency change ($-\Delta\text{Hz}$) at various RH values for TBHC and NTBHC thin films.

Table 1

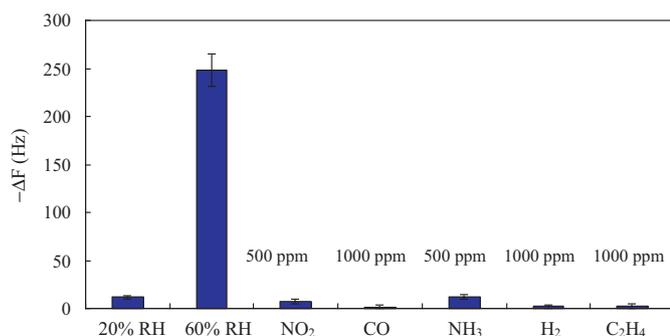
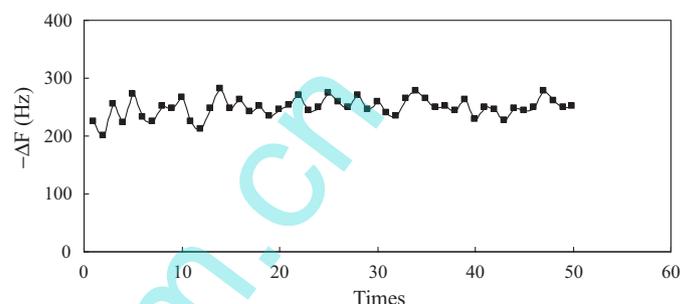
The sensitivity and linearity of the TBHC and NTBHC thin films that were coated on QCM at various RH values.

	Sensing characteristics			
	20–70% RH		20–90% RH	
	Slope (log Z/% RH) ^a	Correlation coefficient (R ²) ^b	Slope (log Z/% RH) ^a	Correlation coefficient (R ²) ^b
TBHC	3.776	0.8912	9.217	0.7900
NTBHC	5.140	0.9621	6.004	0.9679

^a Defined as the slope of linear fitting correlation in the range from 20% to 90% RH.^b Defined as the R-squared value of a linear fitting correlation in the range from 20% to 90% RH.**Fig. 7.** Hysteresis of the humidity sensor. Inset: frequency shifts (Hz) as a function of time (s) between adsorption and desorption processes.

sensor developed herein. The hysteresis (between adsorption and desorption, measured over an RH range of 20–90% RH) was less than 2% RH. Fig. 8 plots the cross-sensitivity effects of NO₂, CO, NH₃, H₂ and C₂H₄ gases on the humidity sensor at 20% and 60% RH. NO₂, CO, NH₃, H₂ and C₂H₄ gases have no significant cross-sensitivity effects on the humidity sensor at 60% RH. However, at testing point of 20% RH, NO₂ (500 ppm) and NH₃ (500 ppm) gases may be regarded as cross-sensitivity effects on the humidity sensor. Fig. 9 plots the stability test, in which the sensor underwent 50 times of adsorption and desorption cycles at testing point of 60% and 20% RH, respectively. The relative standard deviation (RSD) for the humidity sensor was 6.9% during the test.

The sensing difference of humidity sensors of the different batch fabrication is defined as reproducibility and calculated as the coefficient of variation (standard deviation ÷ average × 100%). For three batches of sensors, the reproducibility was 4.2% at testing point of 60% RH. The detection limit (D.L.), calculated as S/N=3 (6 Hz), of the humidity sensor was found to be about 10% RH. The humidity sensing properties of the presented humidity sensor were

**Fig. 8.** Frequency change (–ΔF) of the humidity sensor exposure to various gases for 200 s at 20% and 60% RH.**Fig. 9.** Stability of the humidity sensor at testing point of 60% RH.**Table 2**

Humidity sensor performance of this work compared with literature.

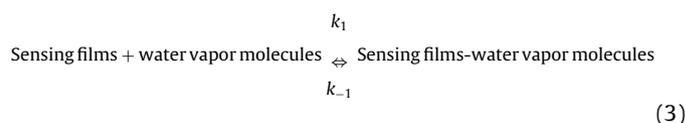
	Literature ^a	This work
Sensing material	Calix[4]arene derivatives with both carboxylate and sulphonate groups	Calix[4]arene derivatives with both benzoyloxy and nitrophenylazo groups
Sensor structure	QCM electrode	QCM electrode
Working range	22–84% RH	20–90% RH
Sensitivity ^b	140,335 (Hz/% RH*μm)	354 (Hz/% RH*μm)
Hysteresis ^c	18% RH	2% RH

^a The data refers to Ref. [13].^b The sensitivity was defined as the frequency change normalized per loading mass of sensing material at testing point of 80% RH.^c The hysteresis was evaluated by the difference in frequency change between humidification and desiccation processes in the working range.

compared with literature [13], as described in Table 2. The hysteresis of the humidity sensor herein was better than that of the sensor that was made from calix[4]arene derivatives with both carboxylate and sulphonate groups. However, the sensitivity of the humidity sensor herein was lower than that was made of the calix[4]arene derivatives with both carboxylate and sulphonate groups.

3.3. Adsorption properties of TBHC and NTBHC thin films

In order to elucidate the increase in sensitivity to humidity of the TBHC and NTBHC thin films, the adsorption dynamics of water vapor molecules onto the TBHC and NTBHC films coated on QCM were investigated. Comparing the adsorption behaviors of water vapor molecules onto TBHC and NTBHC films in Fig. 5, the binding kinetics from the time dependencies of frequency decreases (mass increases) was adopted as the following described [19,20]:



where k_1 and k_{-1} are adsorption and desorption rate constant, respectively. The amount of water vapor molecules, Δm_t , formed

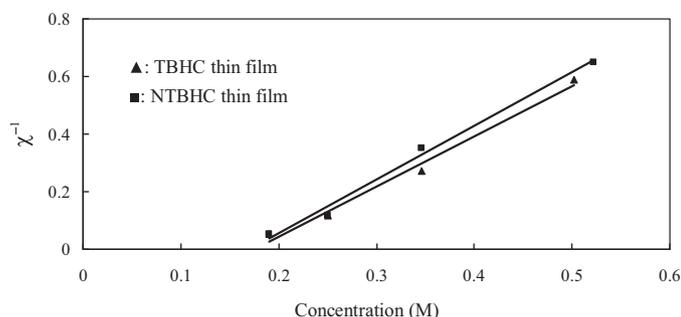


Fig. 10. Linear plot of the reciprocal of relaxation time (χ^{-1}) against water vapor concentration (M) for TBHC and NTBHC thin films.

Table 3
Kinetic parameters for adsorption and desorption of water vapor molecules onto the TBHC and NTBHC thin films.

Thin films	Adsorption rate constant, k_1 ($M^{-1} s^{-1}$)	Desorption rate constant, k_{-1} (s^{-1})	Association constant, K (M^{-1})
TBHC	1.745	0.305	5.719
NTBHC	1.859	0.315	5.897

on the sensing films at time t , is then given by the following equations under Langmuir isotherm adsorption conditions [19,20]:

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

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

where Δm_∞ denotes the maximal amount of water vapor molecules adsorbed on the sensing films at $t \rightarrow \infty$ and χ is relaxation time. Adsorption time courses at different concentrations (0.18–0.50 M) were derived using Eqs. (4) and (5). Fig. 6 plots the linear correlation between reciprocal relaxation time (χ^{-1}) of adsorption and the concentration of water vapor on sensing films (NTBHC and TBHC). Fig. 10 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 NTBHC–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 NTBHC than on TBHC thin film. The association constant K of water vapor molecules onto the NTBHC and TBHC thin films was 5.897 and 5.719 M^{-1} , respectively. Therefore, the larger association constant of water vapor molecules onto the NTBHC thin film than onto the TBHC thin film is associated with the larger adsorption rate constant and the smaller desorption rate constant. Therefore, the NTBHC thin film was more sensitive to water vapor molecules than the TBHC thin film (Table 1).

4. Conclusions

The functionalization of calix[4]arenes can improve the surface properties of calix[4]arenes and the sensitivity of calix[4]arenes to humidity. The NTBHC thin film that was coated on the QCM electrode had high sensitivity (especially at low RH levels), acceptable linearity ($R^2 = 0.9679$) of the relationship between frequency change ($-\Delta f$) and RH in the range 20–90% RH, negligible hysteresis (within 2% RH) and long-term stability, measured at 25 °C. NO_2 , CO, NH_3 , H_2 and C_2H_4 gases have no significant cross-sensitivity effects on the humidity sensor at 60% RH. The NTBHC thin film, combined with QCM, is reliable for measuring humidity.

Based on the Langmuir isotherm adsorption assumption, the adsorption rate constant k_1 for water vapor molecules on NTBHC thin film is larger than that for the TBHC thin film that were coated on QCM. Moreover, molecular mechanics calculations supported the experimental results, indicating that the high sensitivity of the NTBHC thin film to water vapor molecules is ascribed to the larger association constant K of the NTBHC thin film to water vapor molecules than that of TBHC thin film.

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