



Low-humidity sensing properties of PAMAM dendrimer and PAMAM–Au nanoparticles measured by a quartz-crystal microbalance

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ABSTRACT

Low-humidity sensing performance of generation 1 amine terminated polyamidoamine (PAMAM) dendrimer (G1-NH₂), generation 5 amine terminated PAMAM dendrimer (G5-NH₂) and G5-NH₂-Au nanoparticles (G5-NH₂-AuNPs) thin films were investigated by using a quartz crystal microbalance (QCM). The formation of AuNPs was characterized by UV-vis spectrophotometer. The characterizations of the thin films were analyzed by atomic force microscopy (AFM). Water vapor molecules adsorbed onto the G5-NH₂-AuNPs thin film had a larger frequency shift than the G1-NH₂ and G5-NH₂ thin films. Adsorption dynamic analysis, molecular mechanics calculation (association constant), was applied to elucidate how number of amine surface functional groups of PAMAM dendrimer and doped AuNPs in PAMAM dendrimer increase the sensitivity to low-humidity.

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1. Introduction

Low-humidity sensors are adopted extensively in many fields, such as meteorological, agricultural, clinical, and biotechnological fields and manufacturing [1]. Different sensing techniques such as impedance, capacity, optic, field effect transistors (FET), surface acoustic wave (SAW) and quartz crystal microbalance (QCM) have been explored to detect the humidity. Among the above various sensing technologies for humidity detection, the QCM is a very stable device, capable of measuring an extremely small mass change [2]. 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 Δf (Hz) equal to [3]:

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

where f_0 is the foundation resonance frequency of the crystal (Hz), A (cm²) is the surface area of the electrode, and Δm (g) is the change in mass on the surface of the crystal. Therefore, the performance characteristics of QCM-based sensors primarily depend

on the chemical nature and physical properties of the coating materials.

In our earlier studies [4–9], low-humidity sensors were made by coating the single-walled carbon nanotube/Nafion composite material (SWCNTs/Nafion) [4,5], multi-walled carbon nanotube/Nafion composite material (MWCNTs/Nafion) [5], TiO₂ nanowires/poly(2-acrylamido-2-methylpropane) sulfonate (TiO₂ NWs/PAMPS) [6], polypyrrole/TiO₂ nanoparticles (PPy/TiO₂ NPs) [7], MWCNT-COOH and Pd-MWCNT-COOH [8] and poly(4-styrenesulfonic acid-co-maleic acid) (PSSMA) and poly(styrenesulfonic acid) sodium salt (PSS) polyelectrolyte [9] sensing films on an electrode of QCM. These materials include polymers, composites and ceramics, but polymer electrolytes are of particular interest because they have more favorable humidity-sensing characteristics than the other materials, including long-term stability and reliability [10–14].

Polyamidoamine (PAMAM) dendrimers are highly branched well-defined three-dimensional macromolecules with hydrophilic terminal functional groups (-NH₂) [15]. They have attracted much interest recently because of their high geometric symmetry, easily controlled nanosize, controllable surface functionality, film-forming ability and chemical stability, which have resulted in the extension of their use to biosensors and chemical sensors [16–20]. Additionally, Au nanoparticles (AuNPs) have attracted interest owing to their attractive electronic, unique optical, thermal and physical properties as well as their catalytic activity and potential applications in chemical sensors and biosensors [21]. However, no attempt has been made to construct low-humidity sensors based on PAMAM dendrimers. Therefore, in this study, generations 1

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and 5 amine terminated PAMAM dendrimers (G1-NH₂ and G5-NH₂) and G5-NH₂-Au nanoparticles (G5-NH₂-AuNPs) were used to construct QCM-based low-humidity sensors. The surface roughness of the thin films was analyzed using tapping mode atomic force microscopy (AFM). The G5-NH₂-AuNPs were characterized using a UV-vis spectrophotometer. This study investigates how the number of amine surface functional groups and encapsulated AuNPs in PAMAM dendrimers and low-humidity sensing properties are related. Furthermore, the adsorption dynamics of water vapor molecules onto G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films coated on the QCM were employed to elucidate the low-humidity sensing properties (sensitivity).

2. Experimental

2.1. Low-humidity sensor fabrication

2.1.1. Materials

Generations 1 and 5 amine terminated PAMAM dendrimers (G1-NH₂ and G5-NH₂) were obtained from Aldrich as 5 wt% in methanol solution and used without further purification. The preparation of G5-NH₂-AuNPs was similar to the method that was reported by Shi et al. [19]. G5-NH₂-AuNPs were prepared by adding 50 mL of 1.2 mM of HAuCl₄ solution to 0.1 mL G5-NH₂ methanol solution (5 wt%), stirring for 20 min, and then incrementally adding an excess of formic acid (reducing agent, 4.0 mM) into the solution to ensure that most of the HAuCl₄ was reduced to AuNPs. When the AuNPs were formed, the color changed from yellow to wine-red.

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 first rate of 400 rpm for 10 s and second rate of 700 rpm for 10 s, followed by heating at 60 °C for 15 min in air. Consequently, G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films had mass values 2.87, 3.20 and 4.02 μg, respectively, on the QCM disk.

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_v for all experiments. All the measurements were performed at the room temperature 23.0 ± 1.5 °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 formation of AuNPs was characterized by UV-vis spectroscopy (Agilent 8453).

3. Results and discussion

3.1. Characteristics of G5-NH₂-AuNPs

Fig. 2 plots the UV-vis absorption of G5-NH₂-HAuCl₄ solution and G5-NH₂-AuNPs. The G5-NH₂-HAuCl₄ solution had a ligand-metal charge-transfer band at 300 nm (curve a). Curve b is

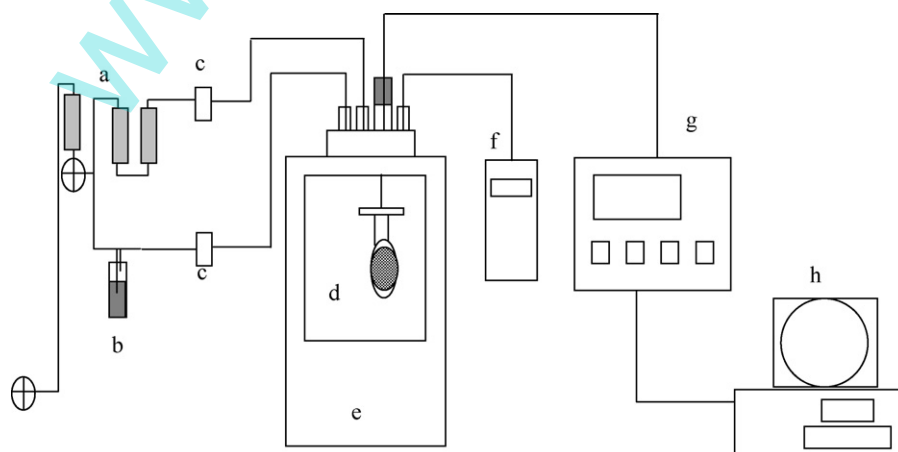


Fig. 1. Schematic diagram of experimental set-up for the QCM sensor measurement and low humidity atmosphere controller. (a) Molecular sieve and desiccating agent; (b) water; (c) mass flow controller; (d) detecting chamber and QCM; (e) thermostat; (f) low humidity hygrometer; (g) oscillator and frequency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

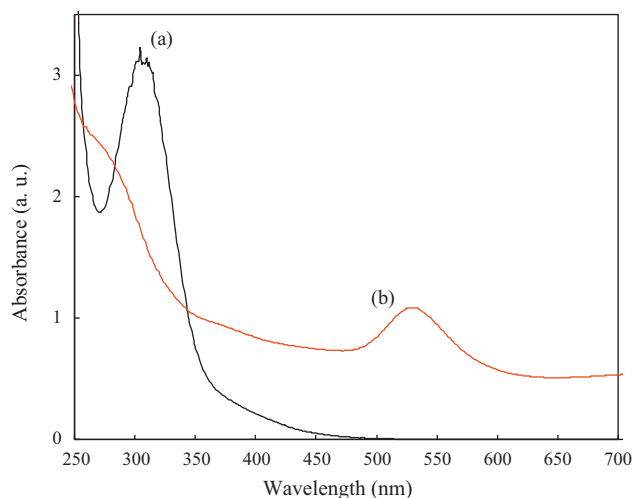


Fig. 2. UV-vis absorption spectra of (a): G5-NH₂-HAuCl₄ solution and (b) G5-NH₂-AuNPs.

the absorption spectra of the after reduction of the G5-NH₂-HAuCl₄ solution using 1.2 mM added HAuCl₄ and formic acid as reducing agent. A maximum absorbance (λ_{\max}) of G5-NH₂-AuNPs was located at 524 nm, resulting from the inter-band transition of the encapsulated AuNPs.

3.2. Surface microstructure characteristics of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films

The surface morphology of PAMAM dendrimers and PAMAM-AuNPs thin films were investigated by AFM. Fig. 3(a)–(c) shows the surface topography of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films, respectively, coated on the QCM. The data of the root mean square (RMS) roughness of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films was 26.6, 27.5 and 31.3 nm, respectively. G1-NH₂ and G5-NH₂ thin films had a smoother surface film than that of G5-NH₂-AuNPs thin film. The deviation (3.8 nm) between G5-NH₂ and G5-NH₂-AuNPs thin films was about 15 times than that of horizontal resolution (0.26 nm). Therefore, obviously different in roughness of the G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films was existed. The difference in surface morphologies between G5-NH₂-AuNPs and G1-NH₂ and G5-NH₂ thin films was due to formation of encapsulated AuNPs in G5-NH₂ and some free AuNPs on the surface of G5-NH₂-AuNPs (Fig. 3(c)).

3.3. Low-humidity sensing properties of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films

Fig. 4 plots the frequency of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films as a function of time for various volume ratios of moist air in the range of 103–2465 ppm_v. Table 1 lists the corresponding sensitivities. The results of calibration curve of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films are plotted in Fig. 5 and the slope and linear correlation coefficient (R^2) were calculated as shown in Table 2. When the volume ratio of moist air was 103 ppm_v, the sensitivity of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films was 0.078, 0.123 and 0.258, respectively (Table 1), demonstrating that the response of the G5-NH₂-AuNPs thin film was higher than those of the G1-NH₂ and G5-NH₂ thin films, especially at low levels of humidity. For G5-NH₂-AuNPs thin film, the linear sensing characteristics at the ranges of 103–1059 ppm_v and 1059–2465 ppm_v show different performance. The steep decrease in slope was observed at the volume ratio of moist air of 1059–2465 ppm_v. Thus, suggesting that addition of AuNPs played an important role in the low humidity sensing property.

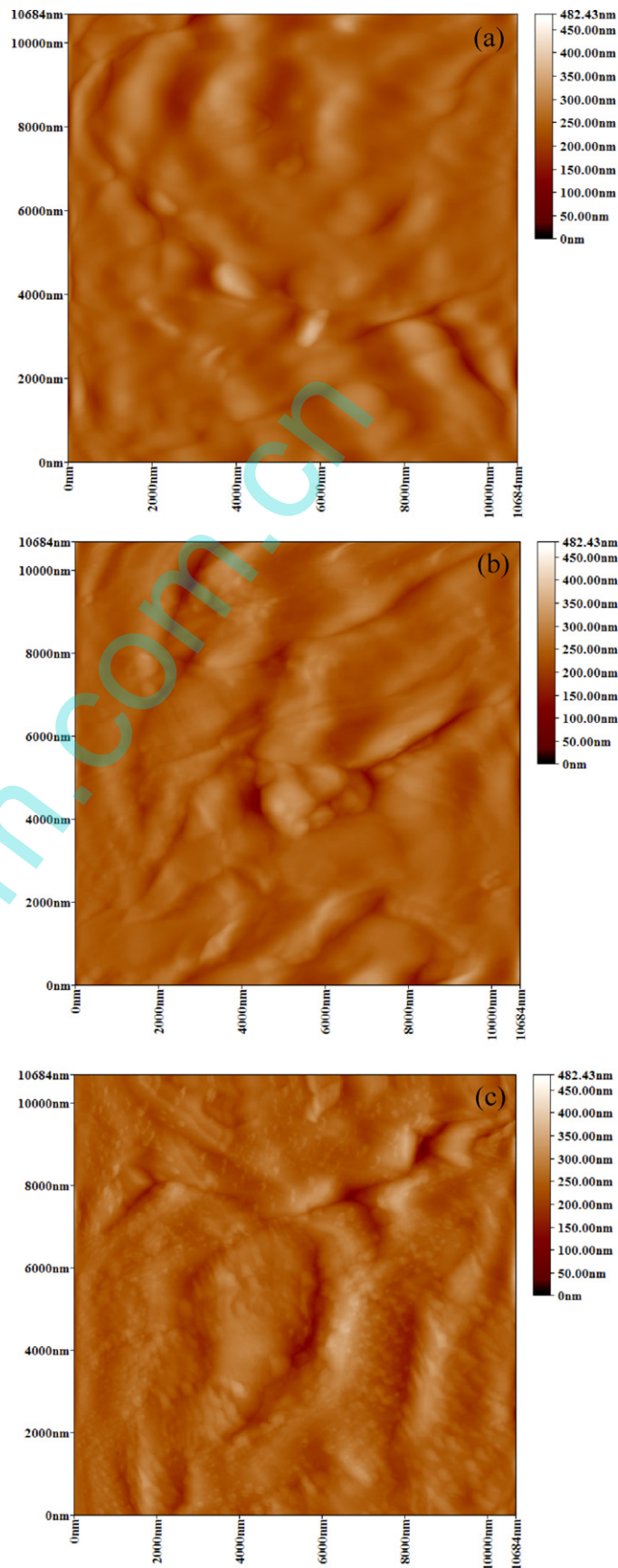


Fig. 3. AFM images of (a): G1-NH₂; (b) G5-NH₂ and (c) G5-NH₂-AuNPs.

Table 1Sensitivity to humidity of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films coated on QCM at different volume ratios of moist air.

Δppm_v^b	Sensitivity ^a		
	G1-NH ₂	G5-NH ₂	G5-NH ₂ -AuNPs
103	0.078	0.123	0.258
436	0.069	0.099	0.200
1059	0.060	0.081	0.166
1733	0.055	0.070	0.141
2465	0.050	0.059	0.121

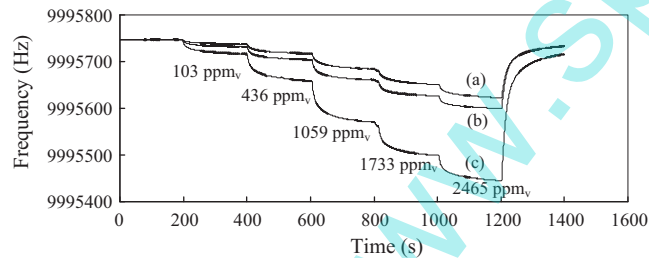
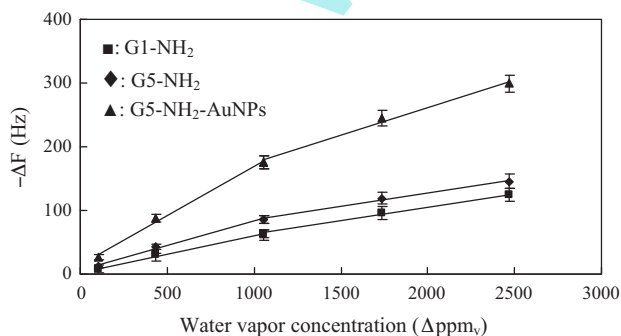
^a The sensitivity of the various sensing films was defined as $-\Delta\text{Hz}/\Delta\text{ppm}_v$ [25].^b The Δppm_v was defined as the volume ratio subtracted by the initial volume ratio of moisture air (2.77 ppm_v).**Table 2**Linear sensing characteristics of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films coated on QCM at different volume ratio of moist air.

	Sensing characteristics			
	103–1059 ppm _v		1059–2465 ppm _v	
	Slope	Linearity ^a	Slope	Linearity ^a
G1-NH ₂	0.0577	0.9974	0.0428	0.9965
G5-NH ₂	0.0757	0.9937	0.0424	0.9921
G5-NH ₂ -AuNPs	0.1539	0.9958	0.0877	0.9909

^a The linearity was defined as the linear regression coefficient of R²-value of linear fitting curve.**Table 3**

Low-humidity sensing characteristics (sensitivity and linearity) of this work compared with the literatures.

Sensing materials	Sensing curve			
	Sensitivity ^a	Linearity ^b	Working range (ppm _v)	References
SWCNTs/Nafion	0.0894	0.9901	154–1052	[4]
MWCNTs/Nafion	0.1782	0.9459	154–1052	[4,5]
TiO ₂ NWs/PAMPS	0.2336	0.9785	207–1038	[6]
PPy/TiO ₂ NPs	0.0128	0.9988	171–1594	[7]
Pd-MWCNT-COOH	0.0541	0.9663	308–1779	[8]
PSS/PAH	0.1199	0.9435	130–1508	[9]
G5-NH ₂ -AuNPs	0.1539	0.9958	103–1059	This work

^a The sensitivity was defined as the slope value of linear fitting curve at the enumerative humidity working range.^b The linearity was defined as the linear regression coefficient of R² value of linear fitting curve at the enumerative humidity working range.**Fig. 4.** Frequency shifts (Hz) as a function of time (s) for different volume ratio of the moist air on (a) G1-NH₂; (b) G5-NH₂ and (c) G5-NH₂-AuNPs thin films.**Fig. 5.** Frequency change ($-\Delta\text{Hz}$) as a function of volume ratio (Δppm_v) for G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films.

The hydrophilic terminal functional groups ($-\text{NH}_2$) of PAMAM dendrimer serve as active sites for water vapor molecules adsorption via the formation of hydrogen (H) bonds. Therefore, the G5-NH₂ thin film had higher sensitivity to humidity than G1-NH₂ thin film, which was attributed to the fact that the number of surface functional groups of G5-NH₂ (128) is higher than that of G1-NH₂ (8) [22]. When G5-NH₂ was modified with AuNPs (Fig. 3(c)), encapsulated AuNPs in G5-NH₂ and free AuNPs formed metallic granules on the surface of G5-NH₂, the number of adsorption sites increased, presenting a high local charge density and a strong electrostatic field, and thereby improved the sensitivity of G5-NH₂-AuNPs than that of the G5-NH₂ thin film. But, at higher volume ratio of moist air (1059–2465 ppm_v), suggested the absence of active sites for reaction to occur and, hence, the steep decreased in slope was observed. The low-humidity sensing properties, based on the sensitivity and the linearity, of the present low-humidity sensor were compared with our earlier studies [4–9] in Table 3. The sensitivity of the present low-humidity sensor was higher than those of the low-humidity sensors made from SWCNTs/Nafion, PPy/TiO₂ NPs, Pd-MWCNT-COOH and PSS/PAH thin films. The linearity of the present low-humidity sensor was comparable to those of the sensors of our earlier studies.

3.4. Adsorption properties of G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films

The adsorption behaviors of water vapor molecules by G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films were compared. The

Table 4
Kinetic parameters for adsorption and desorption of water vapor molecules onto G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs 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})
G1-NH ₂	8.72	0.047	185.5
G5-NH ₂	9.56	0.046	207.8
G5-NH ₂ -AuNPs	14.04	0.040	351.0

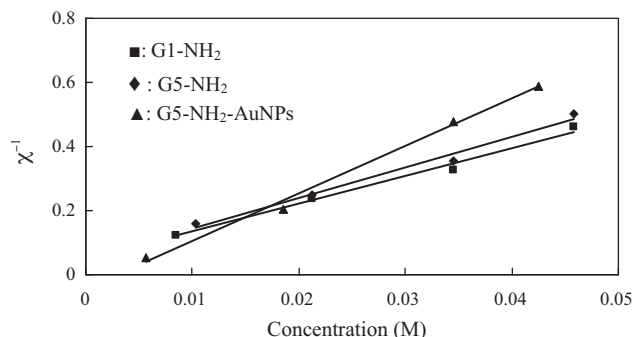
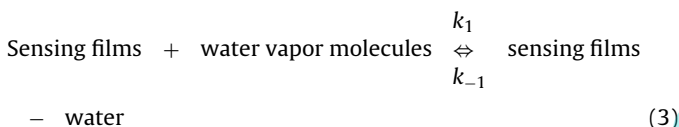


Fig. 6. Linear plot of the reciprocal of relaxation time (χ^{-1}) against vapor concentration (M) for G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films.

following reaction [23,24] explained the increase in sensitivity to low humidity of the G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs thin films.

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



vapor molecules (3) 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 [23,24]:

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

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

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 (0.0057–0.0458 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 (G1-NH₂, G5-NH₂ and G5-NH₂-AuNPs). 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 4). The G5-NH₂-AuNPs – 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 G5-NH₂-AuNPs than on G1-NH₂ and G5-NH₂ thin films. The association constant K of water vapor molecules onto the sensing films was in the following order: G5-NH₂-AuNPs > G5-NH₂ > G1-NH₂. Therefore, the larger association constant ($K = 351.0 M^{-1}$) of water vapor onto the G5-NH₂-AuNPs thin film than onto the G5-NH₂ and G1-NH₂ thin 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 PAMAM dendrimer-based materials plays a predominant role at low-humidity. Therefore, the G5-NH₂-AuNPs thin film was more sensitive to water vapor molecules than the G1-NH₂ and G5-NH₂ thin films (Table 1).

4. Conclusions

The number of surface functional groups (-NH₂) of PAMAM dendrimers dominated the low-humidity sensing properties (sensitivity). The encapsulated AuNPs in G5-NH₂ and metallic AuNPs on the surface of G5-NH₂ can enhance the surface properties of G5-NH₂-AuNPs and increase the sensitivity of G5-NH₂-AuNPs thin film to low levels of humidity. The G5-NH₂-AuNPs coated on the QCM electrode had high sensitivity (especially at low humidity levels) and acceptable linearity. The G5-NH₂-AuNPs 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 G5-NH₂-AuNPs is larger than those for the G1-NH₂ and G5-NH₂ coated on QCM. Moreover, molecular mechanics calculations supported the experimental results, indicating that the high sensitivity of the G5-NH₂-AuNPs thin film to water vapor molecules is ascribed to the larger association constant K of the G5-NH₂-AuNPs thin film to water vapor molecules than those of G1-NH₂ and G5-NH₂ thin films.

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Biographies

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Wen-Hau Tzou received a BS degree in chemistry from Chinese Culture University in 2010. He entered the MS course of chemistry at Chinese Culture University in 2010. His main areas of interest are humidity sensing materials.