

# Low-humidity sensor based on a quartz-crystal microbalance coated with polypyrrole/Ag/TiO<sub>2</sub> nanoparticles composite thin films

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## Abstract

Novel low-humidity sensors were fabricated by the *in situ* photopolymerization of polypyrrole/Ag/TiO<sub>2</sub> nanoparticles (PPy/Ag/TiO<sub>2</sub> NPs) composite thin films on a quartz-crystal microbalance (QCM). The characterizations of the thin films were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The sensitivity increased with the doping amount of TiO<sub>2</sub> NPs. The PPy/Ag/50 wt% of TiO<sub>2</sub> NPs composite thin films exhibited excellent sensitivity (0.0246  $-\Delta\text{Hz}/\Delta\text{ppm}_v$  at 171.1 ppm<sub>v</sub>), linearity ( $R^2=0.9576$ ) and a short response time (12 s at 55.0 ppm<sub>v</sub>). The low-humidity sensing mechanism was elucidated in terms of surface texture and the nanostructural morphology of the composite materials. Additionally, based on the dynamic analysis of adsorption, the association constants of water vapor molecules with PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs composite thin films were estimated to be 81.6 and 227.9 M<sup>-1</sup>, respectively, explaining the effect of adding 50 wt% TiO<sub>2</sub> NPs to PPy/Ag; the sensitivity to low humidity increased as the association constant increased.

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**Keywords:** Low-humidity sensor; Photopolymerization; Quartz-crystal microbalance; Composite material; Polypyrrole/Ag/TiO<sub>2</sub> nanoparticles; Dynamic analysis of adsorption

## 1. Introduction

A serious consumer demand exists for reliable and accurate humidity sensors, especially for use under low-humidity conditions, in meteorological, agricultural, clinical, biotechnological fields and manufacturing applications [1]. New methods and materials are sought to improve upon presently available sensors and detect more accurately the lowest humidity levels.

Conducting polymers such as polythiophene, polypyrrole (PPy) and polyaniline have been intensively studied because of their remarkable mechanical and electrical properties, which are exploited in actuators, sensors and electrochromic devices [2–4]. Among conducting polymers, PPy has attracted much interest because it is easily synthesized, it has relatively high environmental stability and its surface charge characteristics can easily be modified by changing the dopant species in the material during synthesis. However, the PPy prepared by conventional chemical polymerization and electrochemical technique was not

appropriate for use on a nonconducting substrate surface. The main advantage of the photopolymerization process over electrochemical and/or chemical polymerizations is that it allows conducting polymer films to be easily designed and optimized by the incorporation of molecular species into the polymer structure on a nonconducting substrate surface [5].

A quartz-crystal microbalance (QCM) is a very stable device, which can measure an extremely small mass change on the nanogram scale [6]. Therefore, the use of QCM coated with sensitive materials has become an alternative approach for detecting low humidity. The quantitative relationship between the change in frequency  $\Delta f$  (Hz) of the piezoelectric crystal and the mass change caused by mass loading on the piezoelectric crystal surface has firstly derived by Sauerbrey [7]:

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

where  $f_{\text{zero}}$  (MHz) is the basic frequency of the unloaded piezoelectric crystal,  $A$  (cm<sup>2</sup>) is the surface area of the electrode, and  $\Delta m$  (g) is the change in mass on the surface of the crystal. Hygroscopic materials were prepared as films coated on an electrode of QCM to detect humidity. These materials included modified

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nitrate polystyrene [8], Nafion-Ag [9] and polypyrrole [10]. Nanomaterials were also used in sensing films, such as nanosized zeolite films [11], ZnO nanostructure films [12], single-walled carbon nanotube/Nafion composite material [13], multi-walled carbon nanotube/Nafion composite material [14] and TiO<sub>2</sub> nanowires/poly(2-acrylamido-2-methylpropane)sulfonate [15]. However, to our knowledge, no nanocomposite material that is made of nanostructured ceramic materials and conducting polymers has been combined with QCM as a low-humidity sensor. The sensing characteristics of such humidity sensors depend on the microstructure which is determined by the process of fabrication. Not only is sensor material being optimized, but the field of humidity sensor research is also developing approaches for improving the manufacture of sensors for practical applications.

The nanostructured ceramic materials exhibited high humidity sensitivity because they contain capillary nanopores and special surface characteristics [16,17]. Therefore, in this study, low-humidity sensors were made of PPy/Ag/TiO<sub>2</sub> nanoparticles (PPy/Ag/TiO<sub>2</sub> NPs) composite films coated on the gold electrode of QCM by *in situ* photopolymerization. The low-humidity sensing characteristics of PPy/Ag/TiO<sub>2</sub> NPs films were investigated in the volume ratios of moist air from 173.9 to 9711 ppm<sub>v</sub>. The dynamics of adsorption of water vapor molecules on the PPy/Ag and the PPy/Ag/50 wt% TiO<sub>2</sub> NPs films coated on QCM were compared to elucidate the increase in humidity sensitivity of PPy/Ag as TiO<sub>2</sub> NPs are added.

## 2. Experimental

Low-humidity sensors were produced using a method that was similar to that described by Murphy et al. [5] and Srikanth and co-workers [18] and was summarized as a flow diagram in Fig. 1.

### 2.1. Preparation of PPy/Ag/TiO<sub>2</sub> NPs composite materials

The TiO<sub>2</sub> NPs materials (serial number ST-01, 7 nm in diameter) adopted herein were kindly supplied by Ishihara Sangyo Kaisha Ltd. (Japan). The preparation of precursor solution of TiO<sub>2</sub> NPs and the pyrrole (Py) composite was as follows. AgNO<sub>3</sub> (0.03 g, Mallinckrodt Baker Inc.) was added to Py (0.12 g) in ethanol and the mixture was sonicated until the AgNO<sub>3</sub> was completely dissolved; then various weight percentages (0, 10, 30, 40, and 50 wt%) of TiO<sub>2</sub> NPs were added to the solution, which was sonicated to achieve uniform dispersion of nanoparticles.

### 2.2. Fabrication of QCM electrode

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 using 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 1300 rpm for 60 s; the films were then polymerized under UV light (Spectroline, 11SC-1, 254 nm) for 10 min, yielding a black film. As a result, 10, 30, 40, and 50 wt% TiO<sub>2</sub> NPs-doped

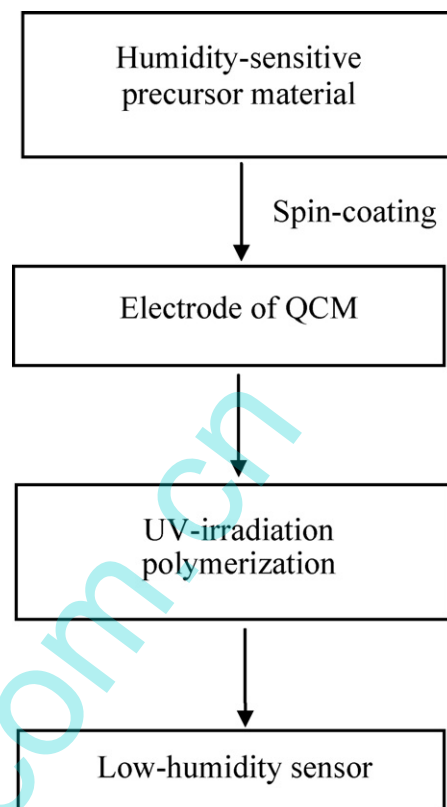


Fig. 1. Flow diagram for the manufacture process of low-humidity sensor.

PPy/Ag composite films had mass values 0.066, 0.146, 0.299, 0.375, and 0.555  $\mu\text{g}$ , respectively, on the QCM disk. The distance between the QCM electrode and the UV lamp was 1.2 cm and the UV intensity was 4.5 mW/cm<sup>2</sup>. Unless otherwise stated, all the measurements were made at room temperature, which was about 23.0  $\pm$  1.5  $^{\circ}\text{C}$ .

### 2.3. Instruments and analysis

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

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

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

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<sub>v</sub> for all experiments.

The surface microstructure and roughness 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 PPy/Ag/TiO<sub>2</sub> NPs composite films

Fig. 2 presents the SEM images of the PPy/Ag/TiO<sub>2</sub> NPs composite films. The TiO<sub>2</sub> NPs were embedded in the PPy/Ag films to yield composite films with 10 wt% added TiO<sub>2</sub> NPs, as presented in Fig. 2a. As presented in Fig. 2b, more naked TiO<sub>2</sub> NPs were present on the surface of the composite film with 50 wt% TiO<sub>2</sub> NPs than on the sample with 10 wt% TiO<sub>2</sub> NPs. Fig. 2c presents the aggregation of TiO<sub>2</sub> NPs.

Fig. 3 presents the AFM images of the PPy/Ag/TiO<sub>2</sub> NPs composite films. The root mean square (RMS) roughness of the PPy/Ag/10 wt% TiO<sub>2</sub> NPs film was about 13.5 nm, as presented in Fig. 3a. Additionally, the RMS roughness of the film with 50 wt% TiO<sub>2</sub> NPs increased to 84.8 nm, as presented in Fig. 3b. The RMS roughness increased with increasing the amount of TiO<sub>2</sub> NPs in the PPy/Ag/TiO<sub>2</sub> NPs film because the TiO<sub>2</sub> NPs were naked. The SEM images reveal this phenomenon (Fig. 2c). All of these factors are responsible for the variation in low-humidity sensing mechanical properties.

#### 3.2. Low-humidity sensing properties of PPy/Ag/TiO<sub>2</sub> NPs composite films

Fig. 4 plots the frequency shifts of PPy/Ag/TiO<sub>2</sub> NPs composite films and a PPy/Ag film as a function of time for various volume ratios of moist air from 173.9 to 9711 ppm<sub>v</sub>. Table 1 lists the corresponding sensitivities. For PPy/Ag/TiO<sub>2</sub> NPs films, the sensitivity increased with increasing the amount of TiO<sub>2</sub> NPs added. The sensitivity of the 50 wt% TiO<sub>2</sub> NPs-doped PPy/Ag film exceeded that of the other samples and the PPy/Ag film. Fig. 5 plots the calibration curves of the PPy/Ag/TiO<sub>2</sub> NPs composite films and the PPy/Ag film. Table 2 presents the slopes and linear correlation coefficients. These results reveal that the added TiO<sub>2</sub> NPs were important to low-humidity sensing. Ceramic and porous materials are known to sense humidity mainly via a surface mechanism [19]. The sensitivity of the PPy/Ag/50 wt% TiO<sub>2</sub> NPs film was higher than that of the PPy/Ag film, to an extent that was related to the adsorption of water molecules on

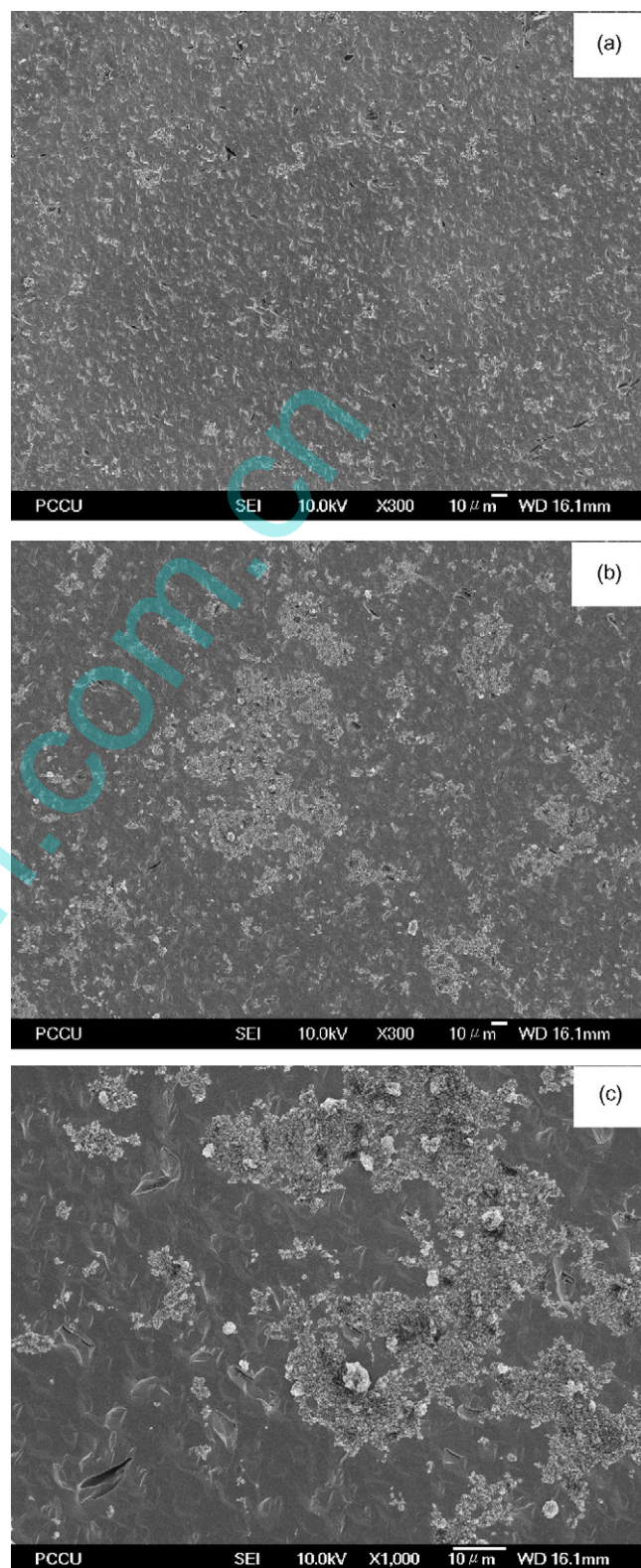


Fig. 2. FE-SEM micrographs of (a) PPy/Ag/10 wt% TiO<sub>2</sub> NPs, (b) PPy/Ag/50 wt% TiO<sub>2</sub> NPs films, and (c) high magnification of PPy/Ag/50 wt% TiO<sub>2</sub> NPs film.



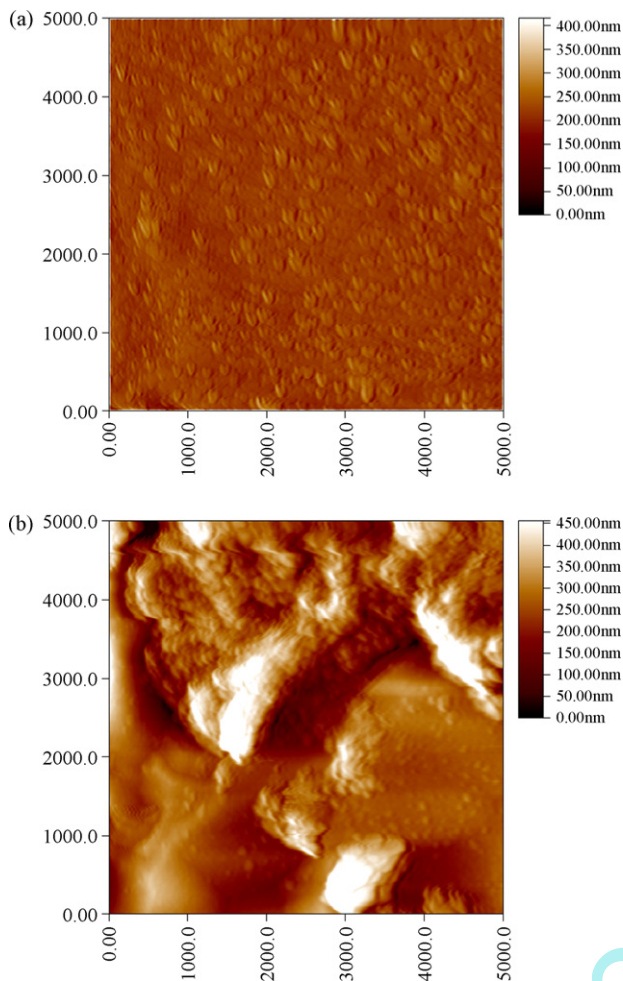


Fig. 3. AFM micrographs of (a) PPy/Ag/10 wt% TiO<sub>2</sub> NPs and (b) PPy/Ag/50 wt% TiO<sub>2</sub> NPs films.

the surface of the composite film. As the nakedness of and the number of defects on the TiO<sub>2</sub> NPs on the surface of the sample with 50 wt% TiO<sub>2</sub> NPs increased (Figs. 2c and 3b), the number of active sites increased (and the specific surface area increased), presenting a high local charge density and a strong electrostatic field, which promoted the dissociation of water on the TiO<sub>2</sub> NPs [17,20].

Fig. 6 plots the results of the adsorption/desorption of water vapors on the PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs coated on

Table 1  
Sensitivity to humidity of PPy/Ag and PPy/Ag/TiO<sub>2</sub> NPs films coated on QCM for different volume ratios of moist air

Volume ratio (ppm <sub>v</sub> )	$\Delta\text{ppm}_v^b$	Sensitivity <sup>a</sup>				
		PPy/Ag	10 wt% TiO <sub>2</sub> NPs	30 wt% TiO <sub>2</sub> NPs	40 wt% TiO <sub>2</sub> NPs	50 wt% TiO <sub>2</sub> NPs
173.9	171.1	0.0114	0.0158	0.0152	0.0187	0.0246
826.7	823.9	0.0044	0.0096	0.0109	0.0138	0.0159
1600	1597	0.0034	0.0080	0.0103	0.0124	0.0140
2656	2653	0.0028	0.0074	0.0092	0.0106	0.0124
4264	4261	0.0020	0.0060	0.0077	0.0087	0.0103
6480	6477	0.0015	0.0057	0.0074	0.0084	0.0090
9711	9708	0.0009	0.0050	0.0058	0.0069	0.0073

<sup>a</sup> The sensitivity of the various sensing films was defined as  $-\Delta\text{Hz}/\Delta\text{ppm}_v$  [8].

<sup>b</sup> The  $\Delta\text{ppm}_v$  was defined as the volume ratio subtracted by the initial volume ratio of moisture air (2.77 ppm<sub>v</sub>).

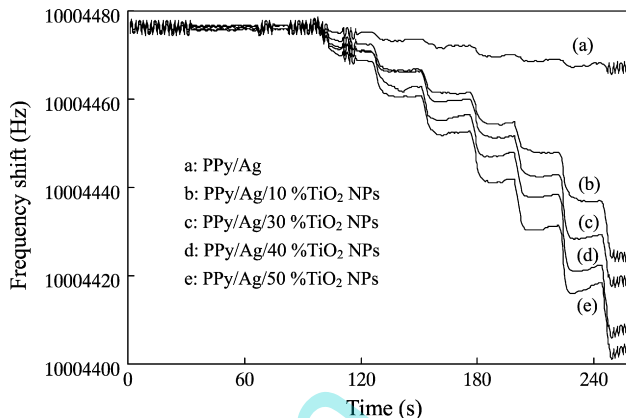


Fig. 4. Frequency shifts (Hz) as a function of time (s) for different volume ratios of the moist air on PPy/Ag and various doped amounts of PPy/Ag/TiO<sub>2</sub> NPs films.

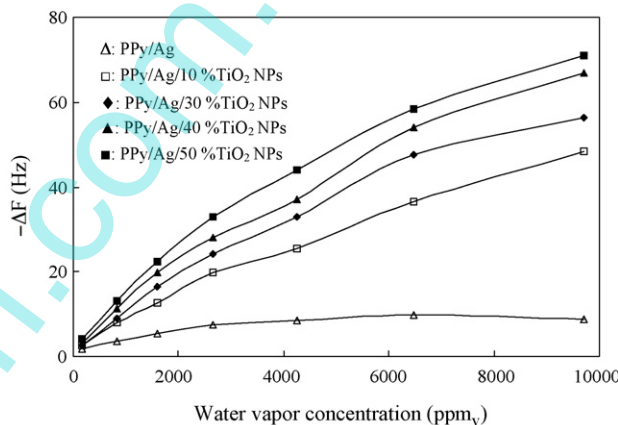


Fig. 5. Frequency changed ( $-\Delta\text{F}$  (Hz)) as a function of water vapor concentration (ppm<sub>v</sub>) for PPy/Ag and various doped amounts of PPy/Ag/TiO<sub>2</sub> NPs films.

QCM at two testing points, 55.0 and 450.0 ppm<sub>v</sub>. The response (RT<sub>90</sub>)/recovery time of PPy/Ag/50 wt% TiO<sub>2</sub> NPs and PPy/Ag films were 12/20 s and 15/18 s, respectively, at the testing point of 55.0 ppm<sub>v</sub>. The adsorption and desorption of water on the PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs films were reversible at two tested water vapor concentrations. Additionally, Table 3 compares the sensing properties of the humidity sensor in this study with those in our previous work [21].

Table 2  
The linear sensing characteristics of PPy/Ag and PPy/Ag/TiO<sub>2</sub> NPs films coated on QCM

	Sensing characteristics	
	Slope	Linearity <sup>a</sup>
PPy/Ag	0.0007	0.6924
10 wt% TiO <sub>2</sub> NPs	0.0047	0.9862
30 wt% TiO <sub>2</sub> NPs	0.0057	0.9623
40 wt% TiO <sub>2</sub> NPs	0.0066	0.9736
50 wt% TiO <sub>2</sub> NPs	0.0069	0.9576

<sup>a</sup> The linearity was defined as the R<sup>2</sup> value of linear fitting curve in the humidity range from 171.1 to 9708 ppm<sub>v</sub>.

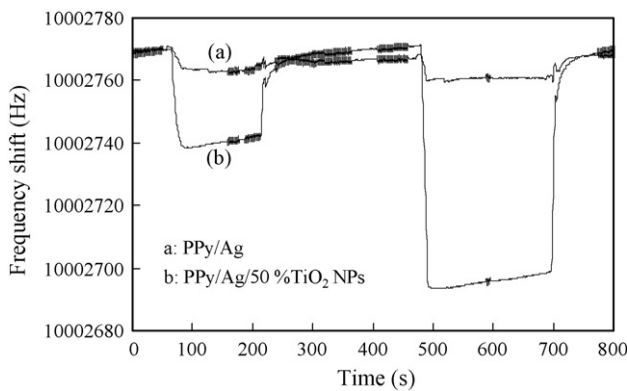


Fig. 6. Reversibility of adsorption of water vapors (55.0 and 450.0 ppm<sub>v</sub>) on PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NP films.

Table 3  
The low-humidity sensor performance of this work compared with previous work

	Previous work <sup>a</sup>	This work
Sensing material	PPy/Ag/TiO <sub>2</sub> NPs	PPy/Ag/TiO <sub>2</sub> NPs
Sensor structure	Comb-like electrodes	QCM electrode
Sensor type	Resistive-type	Mass-type
Working range	30–90%RH	173.9–9711 ppm <sub>v</sub>
Sensitivity	0.0306 log Z%/RH <sup>b</sup>	0.0069 Hz/ppm <sub>v</sub> <sup>c</sup>
Response time	40 s	12 s

<sup>a</sup> The data refers to Ref. [21].

<sup>b</sup> The sensitivity shown as the slope of the sensing curve in the humidity range 30–90%RH.

<sup>c</sup> The sensitivity shown as the slope of the sensing curve in the humidity range 173.9–9711 ppm<sub>v</sub>.

### 3.3. Adsorption properties of PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs films

The behaviors of adsorption of water vapor molecules by the PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs films were compared. The following reaction [9,22] explained the increase in

Table 4  
Kinetic parameters for adsorption and desorption of water vapor molecules onto PPy and PPy/TiO<sub>2</sub> NPs films

Films	Adsorption rate constant, $k_1$ (M <sup>-1</sup> s <sup>-1</sup> )	Desorption rate constant, $k_{-1}$ (s <sup>-1</sup> )	Association constant, $K$ (M <sup>-1</sup> )
PPy/Ag	5.296	0.065	81.61
PPy/Ag/50 wt% TiO <sub>2</sub> NPs	12.72	0.056	227.9

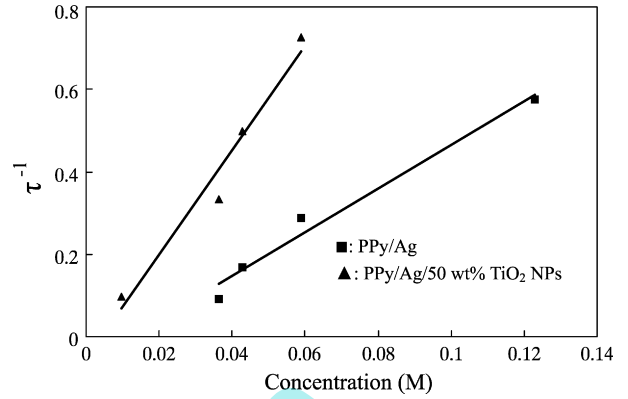
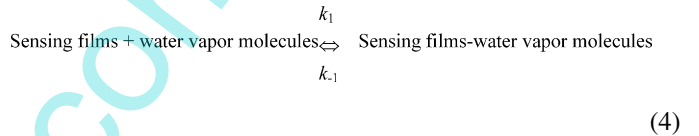


Fig. 7. Linear plot of the reciprocal of relaxation time ( $\tau^{-1}$ ) against vapor concentration (M) for PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs films.

the humidity sensing of the PPy/Ag films with doping with TiO<sub>2</sub> NPs.

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



where  $k_1$  and  $k_{-1}$  are the adsorption and desorption rate constant, respectively. The amount of water vapor molecules,  $\Delta m_t$ , that formed on the sensing films at time  $t$ , is then given by the following equations under Langmuir isotherm adsorption conditions [5,21]:

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

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

where  $\Delta m_\infty$  is the maximal amount of water vapor molecules adsorbed on the sensing films at  $t \rightarrow \infty$  and  $\tau$  is the relaxation time. Adsorption time courses at various concentrations (0.009–0.12 M) were determined using Eqs. (5) and (6). Fig. 7 plots the linear correlation between the reciprocal relaxation time ( $\tau^{-1}$ ) of adsorption and the concentration of water vapor on the sensing films (PPy/Ag and PPy/Ag/50 wt% TiO<sub>2</sub> NPs). Fig. 7 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 the sensing films, all of which are given in Table 4. Additionally, the results in Fig. 6 clearly reveal that the frequency shifts of the PPy/Ag/50 wt% TiO<sub>2</sub> NPs films were the largest. These results reveal that the PPy/Ag/50 wt% TiO<sub>2</sub> NPs film had

a greater affinity for water vapor molecules than the PPy/Ag film. Therefore, the larger association constant ( $K = 227.9 \text{ M}^{-1}$ ) of water vapor onto the PPy/Ag/50 wt% TiO<sub>2</sub> NPs film than onto the PPy/Ag film is associated with the larger adsorption rate constant and the smaller desorption rate constant. Therefore, the PPy/Ag/50 wt% TiO<sub>2</sub> NPs film was more sensitive to water vapor than PPy/Ag (Table 1).

#### 4. Conclusion

The PPy/Ag/50 wt% TiO<sub>2</sub> NPs composite film was fabricated on a QCM electrode by *in situ* photopolymerization. The sensor was highly sensitive especially to low humidity with acceptable linearity, a fast response time and good reversibility. Therefore, the PPy/Ag/50 wt% TiO<sub>2</sub> NPs composite material combined with QCM can be regarded as reliable for measuring trace of humidity.

The Langmuir isotherm adsorption assumption is such that the adsorption rate constant  $k_1$  and the desorption rate constant  $k_{-1}$  for water vapor molecules on PPy/Ag/50 wt% TiO<sub>2</sub> NPs are larger and smaller, respectively, than those for the PPy/Ag film coated on QCM. Therefore, the larger sensitivity of the PPy/Ag/50 wt% TiO<sub>2</sub> NPs film may be attributable to the fact that the association constant  $K$  of the PPy/Ag/50 wt% TiO<sub>2</sub> NPs film with water vapor molecules is higher than that of the PPy/Ag film, because naked and defected TiO<sub>2</sub> NPs have a high local charge density and a strong electrostatic field, which promote dissociation of water on TiO<sub>2</sub> NPs.

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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] E. Smela, Microfabrication of PPy microactuators and other conjugated polymer devices, *J. Micromech. Microeng.* 9 (1999) 1–18.
- [3] R.H.M. van de Leur, A. van der Waal, Gas and vapor detection using polypyrrole, *Synth. Met.* 102 (1999) 1330–1331.
- [4] J.H. Cho, J.B. Yu, J.S. Kim, S.O. Sohn, D.D. Lee, J.S. Huh, Sensing behaviors of polypyrrole sensor under humidity condition, *Sens. Actuators B* 108 (2005) 389–392.
- [5] O.J. Murphy, G.D. Hitchens, D. Hodko, E.T. Clarke, D.L. Miller, D.L. Parker, Method of manufacturing passive elements using conductive polypyrrole formulations, US Patent 5,855,755, (1999).
- [6] A.J. Cunningham, *Introduction to Bioanalytical Sensors*, Wiley, New York, 1998, p. 307.
- [7] G. Sauerbrey, The use of quartz oscillators for weighing thin layers and for microweighing, *Z. Phys.* 155 (1959) 206–222.
- [8] 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.
- [9] 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.
- [10] V. Syritski, J. Reut, A. Öpik, K. Idla, Environmental QCM sensors coated with polypyrrole, *Synth. Met.* 102 (1999) 1326–1327.
- [11] S. Mintova, T. Bein, Nanosized zeolite films for vapor-sensing applications, *Micropor. Mesopor. Mater.* 50 (2001) 159–166.
- [12] 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.
- [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. Actuators 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. Actuators B* 115 (2006) 338–343.
- [15] 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.
- [16] W.P. Tai, J.H. Oh, Fabrication and humidity sensing properties of nanostructured TiO<sub>2</sub>-SnO<sub>2</sub> thin films, *Sens. Actuators B* 85 (2002) 154–157.
- [17] Q. Wan, Q.H. Li, Y.J. Chen, T.H. Wang, X.L. He, X.G. Gao, J.P. Li, Positive temperature coefficient resistance and humidity sensing properties of Cd-doped ZnO nanowires, *Appl. Phys. Lett.* 84 (2004) 3085–3087.
- [18] P. Poddar, J.L. Wilson, H. Srikanth, S.A. Morrison, E.E. Carpenter, Magnetic properties of conducting polymer doped with manganese-zinc ferrite nanoparticles, *Nanotechnology* 15 (2004) S570–S574.
- [19] M.B. Kulwicki, Humidity sensors, *J. Am. Ceram. Soc.* 74 (1991) 697–708.
- [20] R. Schaub, P. Thostrup, N. Lopez, E. Laegsgaard, I. Stensgaard, J.K. Nørskov, F. Besenbacher, Oxygen vacancies as active sites for water dissociation on rutile TiO<sub>2</sub> (110), *Phys. Rev. Lett.* 87 (2001) 266104-1–266104-4.
- [21] P.G. Su, L.N. Huang, Humidity sensors based on TiO<sub>2</sub> nanoparticles/polypyrrole composite thin films, *Sens. Actuators B* 123 (2007) 501–507.
- [22] 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

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