

A humidity sensor based on quartz crystal microbalance using graphene oxide as a sensitive layer

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Abstract

Humidity is a vital physical quantity which is extremely important to production quality control, reliability of electronics, and health of human being etc. This paper proposed a humidity sensor based on quartz crystal microbalance (QCM) using graphene oxide as a sensitive layer, and investigated the characteristics of sensor according to the shift of quality factor (Q factor) as well as resonant frequency at different relative humidity (RH). Results show that at low RH values, the shift of Q factor is more suitable than resonant frequency for assessing the sensitivity than the frequency shift. By combining both frequency and Q factor shifts, we obtained a sensitivity of $\sim 1371/1\%RH$ at 10-60%RH (by Q factor) and $1068 \text{ Hz}/10\%RH$ at 70%RH (by frequency), which are much better than the reported QCM humidity sensors, with good linearity. The QCM humidity sensor also shows good repeatability with response and recovery time smaller than 20 and 3 sec, respectively. These good characteristics of the sensor are attributed to the large surface area and high hydrophilic nature of the graphene oxide, demonstrated good potential for future applications.

Keywords: Quartz crystal microbalance; Graphene oxide; Humidity sensor; Resonant frequency; Q factor

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1. Introduction

Humidity is a vital physical quantity strongly related to human's activities and daily lives. It must be measured and controlled in many fields such as production lines, agriculture, meteorology, space flight and so on. Relative humidity (RH) is the most commonly used parameter, which is defined as the ratio of the partial pressure of water vapor to the equilibrium vapor pressure of water at the same temperature and pressure. Various mechanisms have been utilized to fabricate humidity sensors and commercialized. Among them, humidity sensors based on resistance or capacitance change induced by humidity variation are very popular due to their simple detection methods and relatively high measurement precision[1][2]. However, the yield and reliability of both resistance-typed and capacitance-type humidity sensors are very low. Recently, Quartz crystal microbalance (QCM) humidity sensor has received much attention due to its high sensitivity, good repeatability, short response/recovery time and well-established manufacturing and measurement technologies. QCM device was firstly proposed by Sauerbrey[3], who demonstrated that AT-cut of piezoelectric quartz crystal can be treated as microbalance and developed a relationship between mass change and resonant frequency shift in 1959. The relationship can be expressed by equation (1):

$$\Delta f = -2f_0^2 \Delta m / A(\mu_q \rho_q)^{0.5} \quad (1)$$

where Δf is the change in resonant frequency of quartz crystal due to a mass load of Δm on the surface, f_0 the original resonant frequency, A the active area of crystal, ρ_q the density and μ_q the shear modulus of quartz. To sense humidity, QCM is typically coated with a sensitive or sensing layer, which absorbs different quantities of

water vapor at different RH, leading to different mass loads. Radeva et al. used fullerene as the sensitive layers for QCM humidity sensor in 1997[4], then various nanomaterials have been used as sensitive layers in succession for humidity sensors as their large surface areas could enhance the sensitivity of sensors dramatically. Zhang et al. adopted carbon nanotubes as sensitive layers which were prepared by the spin coating method[5]. The sensitivity of the carbon nanotubes coated sensor was high and the response speed was around 1 min. Su et al. reported a QCM humidity sensor with a double-walled carbon nanotubes (DWNTs) sensitive layer[6], which was used in low humidity environment. Aziza et al. reported a functionalized graphene humidity sensor with good sensitivity, response/recovery, and repeatability[7]. Although carbon nanotubes and graphene flakes are good sensitive layers owing to their large surface areas, the certain degree of hydrophobicity nature of these carbon nanomaterials have suppressed their positive effects on sensitivity. On the other hand, graphene oxide (GO) flakes are a hydrophilic material beside the common nature of nanomaterials[8], and graphene oxide as a sensitive layer is expected to enhance the sensitivity of QCM humidity sensors significantly as demonstrated by flexible and transparent surface acoustic wave based humidity sensors[9]. Yao et al. firstly studied the humidity sensing characteristics of GO on QCM and obtained the relationship between frequency shift and RH [10]. We found that the quality factor (Q factor), which is a dimensionless parameter that describes how under-damped a resonator is and characterizes a resonator's bandwidth (typically 3dB bandwidth) relative to its center frequency, of QCM is also sensitive to RH as well as resonant frequency. In this paper, we propose a QCM humidity sensor with GO as

sensitive layers, and investigate the sensitivity, repeatability, and response speed based on the analysis of both the shift of resonant frequency and Q factor, demonstrating a good prospect in humidity sensing application.

2. Experiments

2.1. Manufacture processes

The proposed QCM humidity sensor used graphene oxide as sensitive layers. Fig.1(a) and (b) are the schematic view and photo of QCM with GO sensitive layers respectively. The QCMs without GO layer, consisting of 166.5 nm thickness AT-cut quartz crystal sandwiched by Au electrodes, were provided by Interquip Electronics Co. (Hong Kong, China) with a resonant frequency of 10 MHz. The processes of preparing a GO layer for QCM humidity sensor are as follows: Firstly, the original QCM was washed in acetone, ethyl alcohol, and deionized (DI) water for 5, 5 and 3 mins respectively by ultrasonic cleaning. Then, the QCM was dried by nitrogen gas, and baked at 60 °C for 10 min. The initial GO dispersion had a concentration of 2 mg/ml, it was diluted by DI water at a ratio of 1:40. A GO sensitive layer was deposited on the surface of the Au electrode of the QCM with the thickness of 400 nm by dispensing GO solution drops on the surface and dried in air at room temperature. After the GO solution on electrode dried out, we obtained a QCM humidity sensor with a GO sensitive layer. The thickness of GO layer was measured by the profilometer (Veeco Dektak 150) as shown in our previous paper [11].

Instead of using a commercial QCM measurement setup, we used a home-made

measurement system for measurement as shown in Fig.1(c), where QCM humidity sensor was put in the air tight testing chamber which has an inlet and an outlet for passing N_2 and a SMA(SubMiniature version A) port for connecting the E5071C network analyzer and the sensor device. The spectrum of resonant frequency and Q factor of device can be obtained by measuring the scattering parameter (S_{11}). The humidity level in the testing chamber can be changed by adjusting the flow ratio from dry N_2 to wet N_2 . The gas flow rates were calibrated and measured by commercial flowmeters (FC-2960M, Tylan). A hygrometograph (BK8321, Bokles) was connected to the testing chamber to measure the relative humidity in chamber in real time for comparison. A LabVIEW (National Instruments Inc.) based program was developed on PC to implement automated measurements of recording both the changes of QCM humidity sensor's resonant frequency and Q factor in real time.

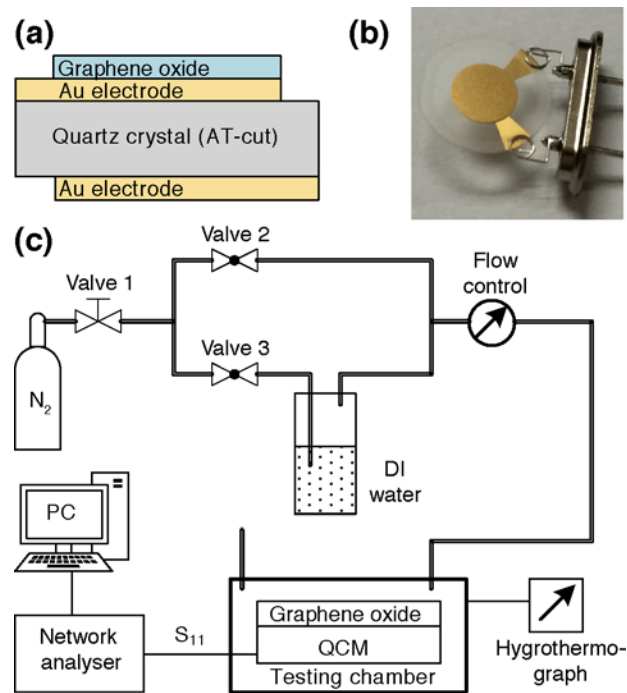


Fig.1 (a) Cross-section schematic view and (b) photo of QCM with GO layer; (c) schematic view of the testing system used for humidity sensing.

2.2. Sensitivity and linearity

Sensitivity and linearity are important parameters to a sensor, and they were evaluated by measuring the shift of resonant frequency and Q factor with varying the relative humidity from 10% to 80% gradually in a step of 10%. Since it was not easy to achieve low RH, the starting value was 11.5%, and was followed at 20%, 30%, and so on. The environment temperature was fixed at 23.3°C. The changes of QCM humidity sensor's resonant frequency and Q factor were automatically measured and recorded by LabVIEW.

2.3. Repeatability and response speed

Repeatability and response speed are also important parameters and need to be characterized always. We chose 20% RH and 23.3°C as a standard condition to measure the resonant frequencies of QCM humidity sensor. Then, we changed the relative humidity, and obtained the new set of resonant frequency, then let the humidity in testing chamber return to 20%, and recorded the resonant frequency again. By repeating the above operations, the curve of resonant frequencies was automatically recorded by LabVIEW, and the repeatability and response speed of sensor were then evaluated.

3. Results and discussion

3.1. Sensitivity and linearity

The resonant frequency of the QCM humidity sensors without and with a GO layer is 10,087,533 and 10,087,457 Hz, respectively, at 20% RH and 23.3 °C. The decrease

of frequency of 76 Hz is due to the mass loading of the GO layer on the surface, corresponding to a mass of 400 nm thickness GO film. The resonant frequencies of the QCM humidity sensor with and without GO layer at different humidity levels are showed in Fig.2 as a function of time. The blue curve with solid triangle symbols is the measured relative humidity showing in the right Y-axis. The resonant frequencies of QCM with and without GO are referred to the left Y-axis. The surface of the QCM crystal is Au. Although it is hydrophilic, the flat surface has limited ability to absorb moisture from the environment, and the frequency shift caused by 80%RH humidity is still very small. Adding a GO layer increases the frequency shift significantly, and is attributed to the remarkably increased surface area of the nanomaterial sensing layer and hydrophilic property.

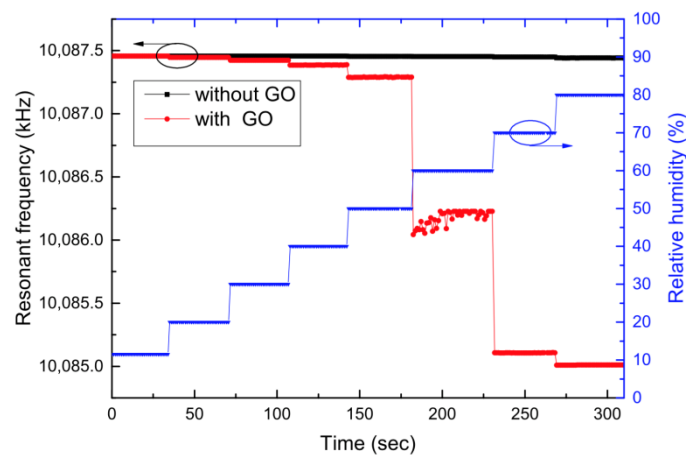


Fig.2.Comparison of resonant frequency shift for QCM with and without GO to the RH changing from 10% to 80% in step.

The frequency shift is quite different at different RH values. The frequency shift is only a few tens of Hz per 10%RH increment for the humidity between 10%RH and 50%RH, while it changes more than 1,000 Hz per 10%RH increment between 50%RH and 70%RH. The reason is that the speed of the water molecules absorbed on the

graphene oxide is faster at higher humidity, so that the resonant frequency decrease (Δf) becomes larger with the increase of relative humidity. The fluctuation of the red curve at about RH=50% was caused by experimental error due to unstable gas flow. It can also be seen in Fig.2, when the humidity increases from 70% to 80%, the resonant frequency shift becomes small as well, changes only about 100 Hz. It is believed that the graphene oxide sensitive layers have saturated with absorbed water molecules when the relative humidity is higher than 70%.

Humidity sensitivity (S) is a measure always used to assess humidity sensors, it is defined by a shift of frequency, Δf , against a humidity change as [10] :

$$S = \frac{\Delta f}{\Delta RH} \quad (2)$$

where ΔRH is the change of relative humidity. The evaluated S and Δf are shown in Fig.3 as a function of RH value. Since the speed of the water molecules absorbed by the graphene oxide is faster and the volume of the graphene oxide expands quicker at higher humidity levels [12], the decrease of resonant frequency becomes larger at higher humidity. This results in higher sensitivity when the humidity is greater than 50%RH. The sensitivity is as large as 1114 and 1068 Hz/10%RH at 60% and 70%, respectively, while that of reported carbon nanotube QCM humidity sensor is only a few hundreds of Hz/10%RH[5]. Therefore, the proposed QCM humidity sensor's sensitivity is much better compared with the reported QCM humidity sensors, and this is attributed to the large specific surface area and hydrophilic nature of the graphene oxide layers. The sensitivity is also related closely to the thickness of graphene oxide layers, and can be significantly enhanced with the increase of graphene oxide layer thickness[9].

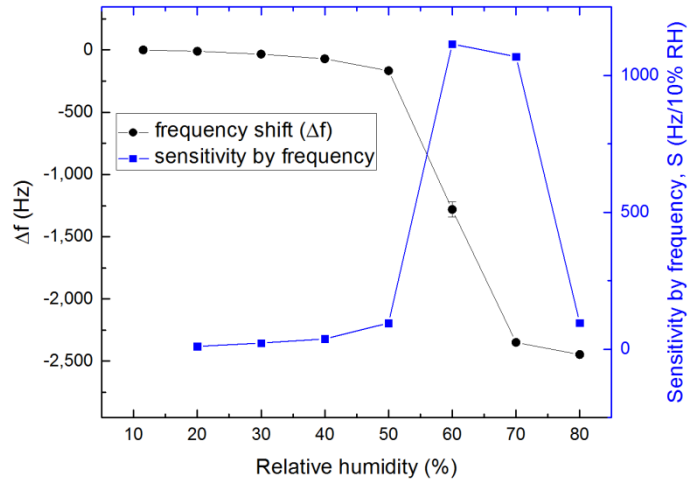


Fig.3. Resonant frequency shift and evaluated sensitivity as a function of relative humidity.

As can be seen in Fig.3, the sensitivity of the QCM sensor with GO is high at medium RH values, but low at low RH values, and the linearity of Δf and S are also poor, which limited the use of the sensor. We investigated the relationship between Q factor and RH, and found that the shift of Q factor with RH has much better linearity than the shift of resonant frequency with RH at low humidity, which is shown in Fig.4.

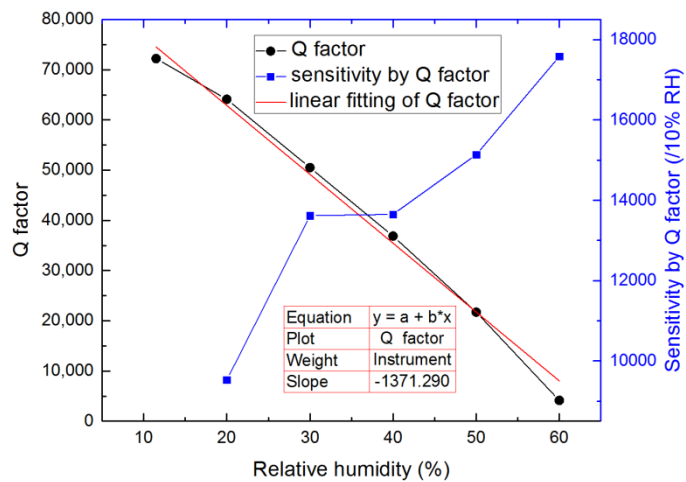


Fig.4. Q factor shift and evaluated sensitivity as a function of relative humidity.

At a RH level of 11.5%RH, the QCM has a Q factor of 72,229, and it decreases with the increase of RH level up to 60% with a good linearity with a gradient of about 1371/1%RH. Beyond 60%RH, the Q factor becomes smaller, not particularly suitable

for sensing application. We defined a sensitivity by Q factor as $\Delta Q / \Delta RH$, the relationship between the sensitivity by Q factor and humidity can be obtained as shown in Fig.4 by the right Y-axis. It increases with humidity level and reaches the maximum of 17580 /10% RH at 60%RH, showing better linearity than the sensitivity by frequency in Fig.3. The reason why Q factor is more sensitive than resonant frequency at low RH value may be attributed to the high Q factor of original QCM and the fact that the damping of acoustic wave in water is more serious than the mass load effect at low humidity environment. At low RH, the absorbed moistures are few, leading to low mass load effect, but for acoustic transmission, the absorbed moistures are sufficient to introduce relatively severe acoustic loss, resulting in large decrease of Q factor. Combining the shift of resonant frequency and Q factor, the QCM with GO sensing layer provides good sensitivity and linearity from low to medium RH values.

3.2. Repeatability and response speed

The result of repeatability measurement is shown in Fig.5. As can be seen, the resonant frequency of the QCM humidity sensor is about 10,087.46 kHz at 20%RH, when the relative humidity increases in the test chamber, the resonant frequency of the QCM humidity sensor decreases. When the relative humidity returns to 20%, the resonant frequency returns to 10,087.46 kHz, demonstrated a good repeatability. We define the rise time as the time required for the frequency response to rise from 10% to 90% of its final value when the RH changes from high value to 20%RH and the same for the fall time when RH changes from 20%RH to high value. It can also be seen in Fig.5, the response speed when switching from high RH to low RH (recovery time) is

smaller than 3 sec, while the fall time (response time) is about 20 sec, both of them are much better than the reported humidity sensors [13]. Graphene oxide is a layered material, consisting of hydrophilic oxygenated graphene sheets bearing oxygen functional groups on their basal planes and edges[8], therefore the response speed of the QCM humidity sensor using graphene oxide as sensitive layers is very fast. The performance of the present sensor and reported work are summarized in Table 1 for comparison.

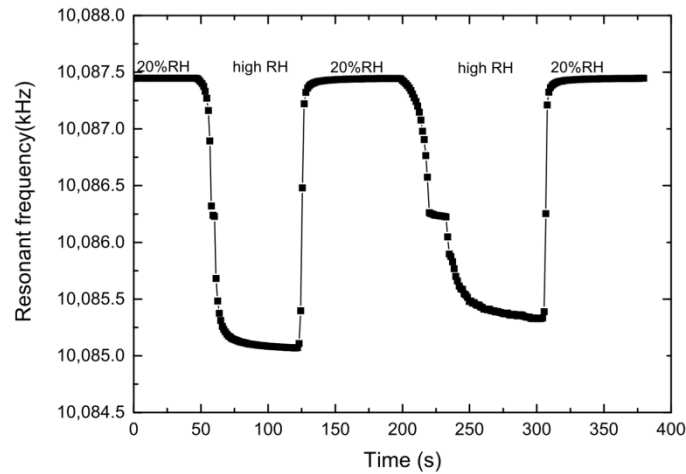


Fig.5. Resonant frequency of QCM with GO layer as relative humidity changed repeatedly.

Table 1

Comparison between sensor in this work and reported work

Reference	Sensitive material	Sensing range	Sensitivity	Response time (s)	Recovery time (s)
This paper	GO	10~60%	1371(Q)/1%RH	20	3
		60~70%	1068 Hz/10%RH		
[4]	fullerene	30~70%	11 Hz/1%RH	not given	not given
		70~90%	30 Hz/1%RH		
[5]	carbon nanotube	5~97%	12.5~47.1/%RH	60	70
[10]	GO	6.4~93.5%	max: 22.1 Hz/%RH	18-45	12-24
[13]	GO/ethyleneimine	11.3~97.3%	27.3 Hz/%RH	53	18
[14]	ZnO	5~96.9%	55.5~90.9 Hz/%RH	90	120
	nanostructure				
[15]	ZnS nanowire	45~90%	2.1 Hz/%RH	14	18

4. Conclusion

We proposed, manufactured, and characterized QCM humidity sensors using graphene oxide as a sensitive layer. The shift of Q factor was investigated at various conditions as well as the resonant frequency for characterizing the sensor. Results showed that shift of Q factor is suitable for assessing sensing performance of the sensor at low humidity, while the shift of frequency is more suitable for assessing the performance at medium humidity. The sensor shows good sensitivity, linearity, repeatability, and fast response speed. A sensitivity of $\sim 1371/1\%RH$ at 10-60%RH (by shift of Q factor) and $1068Hz/10\%RH$ at 70%RH (by shift of frequency) have been achieved, which are much better than the reported QCM humidity sensors. The QCM sensor shows a good prospect for future application.

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Fig.4 Q factor shift and evaluated sensitivity as a function of relative humidity.

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