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Impedance analysis of quartz crystal microbalance humidity sensors based on nanodiamond/graphene oxide nanocomposite film

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ABSTRACT

In this work, detonation nanodiamond (DND)/graphene oxide (GO) nanocomposites with various weight ratios were prepared. By combining with quartz crystal microbalance (QCM) technique, the humidity sensing properties of these nanocomposites sensors, including response sensitivity, humidity hysteresis, dynamic response and recovery, were studied through an impedance analysis method. The test results indicated that DND/GO nanocomposites showed high humidity response sensitivity, logarithmic linear response, fast response/recovery and small humidity hysteresis. Moreover, the influence of DND content in nanocomposite on the humidity response sensitivity and quality factor of the sensors has also been discussed. The results revealed that the increase of DND content in nanocomposite could enhance the humidity response sensitivity, but reduce the quality factor of the sensor. So, it is very necessary to select a suitable DND content in nanocomposite for balancing the sensitivity and quality factor. In addition, the reasons for the enhanced humidity sensing performance have also been discussed in detail. This work demonstrated that DND/GO nanocomposite is a promise candidate material for humidity sensing detection by combing with QCM technique.

1. Introduction

The accurate and reliable detection of relative humidity have attracted a great deal of attention in the fields of meteorology, agriculture, electronics, food storage, etc. [1,2]. The increasing demand of humidity sensor market promotes a large number of efforts to fabricate high performance humidity sensor. So far, a variety of transduction mechanisms, including capacitive [3,4], resistive [5], gravimetric [6], optical [7], strain [8], etc., have been explored to develop humidity sensor. Among the existing mechanisms, humidity sensor using quartz crystal microbalance (QCM) technique has become more and more popular since the first report by King [9]. The advantages of QCM humidity sensor include high sensitivity, low cost, digital frequency signal output and excellent stability [10]. The QCM humidity sensor is generally composed of a QCM transducer and a layer of sensitive material deposited on the electrode of QCM. The adsorption of water molecules onto sensitive material will make QCM yield a frequency response. Until now, many researchers have already devoted themselves to enhance humidity response sensitivity by developing various kinds of humidity sensitive materials. Beside humidity response sensitivity, the stability of QCM humidity sensor, which is quantitatively described by quality factor (*Q*-factor), is also an important characteristic for evaluating sensor performance. In most cases, the sensitive materials used for QCM humidity sensor are not purely rigid. The introduction of the viscosity of non-rigid sensitive material, on one hand, will increase the sensor sensitivity according to Eq. (1) [11]:

$$\Delta f_{\text{non-rigid}} = -\frac{2f_0\Delta m}{A\sqrt{\rho_q\mu_q}} - f_0^{2/3}\sqrt{\frac{\rho_L\mu_L}{\pi\rho_q\mu_q}} \quad (1)$$

where f_0 is the resonant frequency, Δm is the additional mass on the electrode, A is the surface area of the electrode, ρ_q and μ_q are the density and shear modulus of quartz, ρ_L and η_L are the density and viscosity of sensitive material, respectively. On the other hand, the increase in viscosity of non-rigid sensitive material during water adsorption will damp the QCM and reduce the *Q*-factor of the sensor. So, it is very essential to pay special attention to the change of *Q*-factor besides response sensitivity.

In the last two decades, nanostructure sensitive materials, especially nanocarbon materials, have already shown a great prospect in the field of gas/humidity sensor. Compared with bulk materials, nanostructure sensitive materials usually exhibit some obvious advantages for sensor application, such as large specific surface area, outstanding adsorption capacity, high mechanical stiffness

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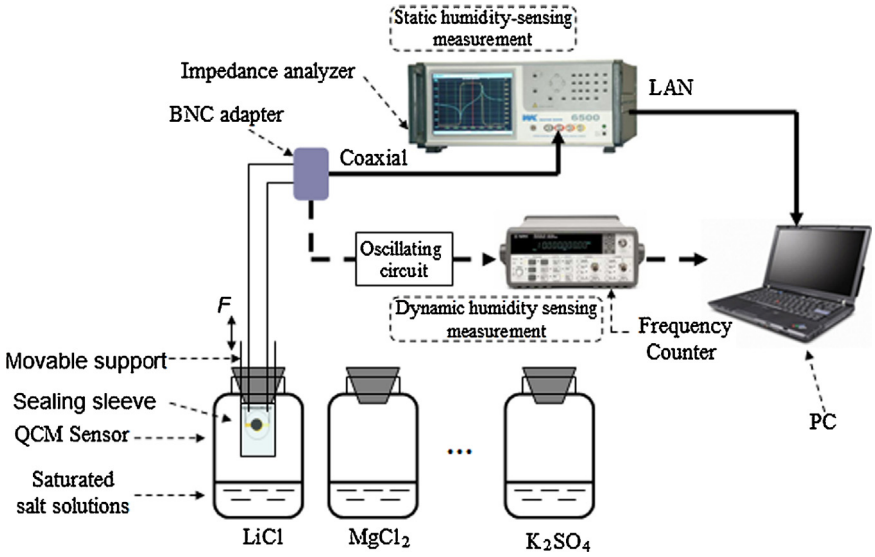

Fig. 1. Schematic diagram of humidity sensing experimental setup.

Table 1
BET surface area analyses of GO and DND/GO nanocomposite ($R = 1$).

Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
GO	10.333	0.011	3.713
DND/GO ($R = 1$)	49.573	0.109	3.939

and satisfactory stability. Up to now, a variety of carbon nanostructure materials, including zero-dimensional fullerenes (C_{60}) [12], one-dimensional carbon nanotube (CNT) [13] and two-dimensional graphene oxide (GO) [14], have been used for humidity sensor by combining with QCM. Among the three kinds of carbon nanostructure materials, GO is a promise candidate material for high precision detection of humidity. Our pervious studies demonstrated that GO based QCM humidity sensors displayed both large humidity response sensitivity and high frequency stability [10,14]. Su and Kuo [6] experimentally compared the humidity response sensitivities of GO and CNT based QCM humidity sensors, and found that the sensitivity of GO based QCM humidity sensor was better than that of CNT based QCM humidity sensor. However, it is noteworthy that GO sheets should be aggregated to form a relatively compact film after drying. This property heavily reduces the specific surface area contributed by individual GO sheets. To address this drawback, a few studies presented a new approach to introduce nanoparticles into GO sheet for preventing the agglomeration of GO sheets in the process of drying [15,16]. The GO/nanoparticles composite film displays microporous-layered nanostructures, and thereby can provide large specific surface area [15]. This approach is beneficial to acquire high sensor's response sensitivity.

Detonation nanodiamond (DND) with typical sizes in the 5–10 nm range has recently been extensively concerned in the areas of tribology, biology and sensitive electronics due to its excellent mechanical properties, high surface areas and tunable surface structures [17]. The rich surface groups of DND, such as hydroxyl and carboxyl groups, make DND expediently realize functionalization with other sensing material [17]. In this work, we considered to synthesis DND/GO nanocomposite and examine its humidity sensing properties by combining with QCM technique. The sensor performances, including humidity response sensitivity, humidity hysteresis, dynamic response and repeatability of the sensors, were experimentally studied. In addition, the effect of DND content in nanocomposite on humidity sensing performances was also discussed.

2. Experimental

2.1. Preparation of GO/DND composites

Graphite oxide was synthesized by the oxidation of natural graphite powder by a modified Hummers method [18]. Subsequently, single-layered GO sheets were achieved by the exfoliation of graphite oxide under ultrasonication in water. The concentration of the prepared GO dispersion was 1 mg/mL. DND powder with typical sizes in the 5–10 nm range was purchased from Nanjing Xianfeng Nano Co. Ltd. China. Based on its excellent hydrophilic property, DND can be readily dispersed in water. Then, 2.5, 5 or 10 mg of DND powder was added into 10 mL GO dispersion (1 mg/mL), respectively. Successively, these mixtures were treated via ultrasonic treatment for 1 h for obtaining homogeneous

Table 2
The equivalent circuit elements parameters of DND/GO nanocomposite based QCM sensor at various humidity points.

RH	Equivalent circuit elements parameters									
	DND/GO nanocomposite sensor ($R = 4$)					DND/GO nanocomposite sensor ($R = 1$)				
	R^* (Ω)	L^* (mH)	C (fF)	C_0 (pF)	Q	R^* (Ω)	L^* (mH)	C (fF)	C_0 (pF)	Q
11.3%	7.72	26.27	9.66	7.38	78,243	100.56	25.39	10.00	7.60	6348
32.8%	7.86	26.26	9.66	7.35	76,938	100.35	25.47	9.97	7.36	6170
54.3%	8.25	26.22	9.68	7.39	73,649	135.13	25.50	9.96	7.16	4465
75.3%	8.99	26.21	9.68	7.52	67,645	186.35	25.17	10.09	7.45	3235
84.3%	10.21	26.29	9.63	7.69	61,213	238.15	25.32	10.02	7.65	2555
97.3%	12.76	26.55	9.56	8.32	45,951	287.03	25.51	9.96	8.00	2144