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A highly linear humidity sensor based on quartz crystal microbalance coated with urea formaldehyde resin/nano silica composite films

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ABSTRACT

A highly linear humidity sensor based on a quartz crystal microbalance (QCM) was developed using urea formaldehyde resin (UFR) and nano-silica composite films. The composite films were prepared by in situ polymerization on the surface of the quartz crystal electrode. The scanning electron microscopy (SEM) images show that there are some interaction between UFR and nano-silica in the blend. The experiment results indicate that the optimal mass ratio of urea and formaldehyde to nano-silica is 1:2.8 and the total mass of the composite films loaded on the QCM is 0.95 μg. Under the optimum conditions, the humidity sensor exhibits good linearity (R^2 = 0.9998), short response time (12 s), short recovery time (25 s), good stability and reproducibility. The proposed sensor can be applied to the determination of humidity in practical production.

1. Introduction

Humidity measurement and control are very important in many areas, such as weather forecast, food processing and storage, agriculture, automobiles, etc. Therefore, humidity sensor has been extensively studied. According to different sensing techniques for the determination of humidity, the humidity sensors can be mainly categorized into capacity [1,2], impedance [2,3], optics [4,5], surface acoustic wave (SAW) [6–8], quartz crystal microbalance (QCM) [9–11], etc. Among the sensing techniques above, QCM detectors have a low detection limit and wide measuring range [10]. The performance of the QCM sensor mainly depends on the properties of coating material. Recently, many sensing materials were prepared as films coated on the electrode of QCM to measure humidity, such as nitrated polystyrene [9], Nafion-Ag [10], CNTs/Nafion [11–13], nanosized ZnO [14–18], polyelectrolyte [19,20], polysiloxane [21], calcein [22], gold nanoparticles [23], mesoporous silica SBA-15 [24], PDDA/PSS [25], polypyrrole [26], TiO_2 nanowires/soluble polymers composite material [27], and arene derivative [28]. QCM humidity sensors based on composite materials as sensitive films have already become a research hotspot due to their high sensitivity. The composite material can be divided into two main types. One is that the nano-material is used as skeleton and the polymers with hydrophilic groups cover on the surface of nano-material [10–13,27]. The polymers play a major role of absorbing water. The other is that two kinds of material are both sensitive material [29]. However, poor linearity may be obtained at high humidity using above composite materials. Our group had reported a novel QCM humidity sensor which sensitive polymer was urea-formaldehyde resin (UFR) polymer. It was prepared by in situ polymerization on the quartz crystal electrode in acidic conditions [30]. The frequency shift of the proposed sensor changes sensitively with relative humidity and the developed sensor exhibits good reproducibility and stability. Unfortunately, the absolute value of frequency shift of per unit humidity is little under the condition of low humidity, while the absolute value of frequency shift is big under the condition of high humidity. As one of the ultrafine inorganic materials, nano silica has several advantages such as: specific surface area, surface adsorption force, surface energy, high chemical purity and good dispersion performance. It can be used as sensing material of humidity sensor due to lots of hydroxyl groups on the silicon surface [24]. In contrast to the UFR film, the absolute value of frequency shift of per unit humidity is big under the condition of low humidity, while the absolute value of frequency shift is little under the condition of high humidity [31]. In addition, nano-silica is also difficult to be immobilizated alone on the surface of the QCM electrode, which prevents it from being applied for the purpose of humidity sensor.

Herein, the aim of this work was to fabricate a humidity sensor with good linearity based on QCM coated with UFR/nano-silica composite films. The mass ratio of urea and formaldehyde to nano-

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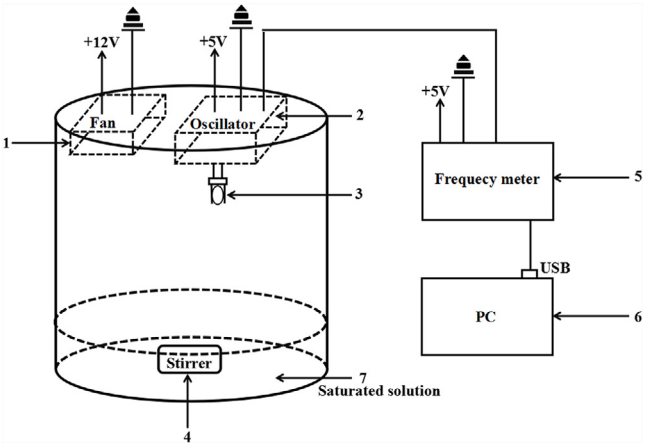

Fig. 1. Schematic diagram of a humidity testing system.

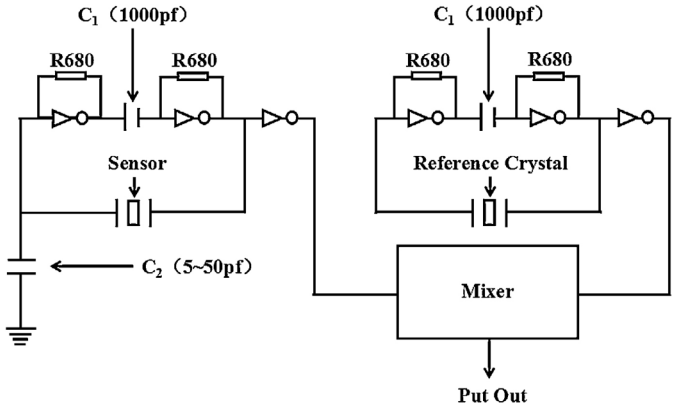

Fig. 2. Oscillator circuit of a quartz crystal microbalance.

silica and the total mass of the composite films which can influence on the linearity of the humidity sensor were investigated in details. The humidity sensing characteristics of the composite films were also discussed, such as the sensitivity, stability, response and recovery times. It is experimentally demonstrated that the QCM coated with the UFR/nano-silica composite films shows a promising application for the determination of humidity.

2. Experimental

2.1. Materials

All the reagents (such as: formaldehyde (37%), urea, nano-silica, $LiCl{\cdot}H_2O$, $MgCl_2{\cdot}6H_2O$, K_2CO_3, NaCl, KCl) involved with analytical grade were bought from Sinopharm Chemical Reagent Co., Ltd. Circular-shaped 20 MHz quartz crystals (consisting of two silver electrodes with a diameter of 3.0 mm and a thickness of ~0.1 mm) were purchased from Pu Tian De Xing Electronic Quartz Co., LTD. Double distilled water was used for preparation of all solutions and for washing.

2.2. Fabrication of UFR/nano silica composite films on QCM

3.0 g of urea (0.05 mol) and 4.9 g of formaldehyde (0.06 mol) were dissolved in 100 mL double distilled water. Solution of the mixtures was stirred for 30 min. The solution was defined as solution (1). 100 μL of solution (1) was first transferred to a 50 mL volumetric flask. Next, a calculated amount of nano silica with different mass ratio of urea formaldehyde resin to nano-silica (1.0:0, 1.0:2.0, 1.0:2.5, 1.0:2.8, 1.0:3.0, 1.0:3.5, 0:1.0) was added under stirring conditions and then the resultant mixture was diluted with double distilled water to volume. The solution was defined as solution (2). Finally, solution (2) was diluted of 8 times with double distilled water. The solution was defined as solution (3).

The silver electrode of the QCM was cleaned ultrasonically in acetone. After drying, 10 μL of solution (3) was added dropwise on both sides of the QCM electrode and then in situ polymerized by heating for 20 min using infrared light to form UFR/nano-silica composite films. The thickness of composite films was controlled by changing the addition volume of solution (3).

2.3. Measurements

The system used for measurement of response to humidity is shown in Fig. 1. The detection system is designed by our team including measure room, double mixing system, oscillation circuit of the QCM (see in Fig. 2), frequency meter, and computer.

The controlled humidity environments were achieved using saturated aqueous solutions of LiCl, $MgCl_2$, K_2CO_3, NaCl, KCl in a closed plastic vessel at an ambient temperature of 25 °C which yielded approximately 11.28, 32.44, 43.17, 75.09 and 83.62% relative humidity (RH), respectively.

The sensor coated with sensing materials was connected to oscillation circuit, and placed on the saturated salt solutions with different relative humidity. When the frequency shift response of the sensor to a relative humidity was stable, the sensor was turned to another saturated salt solution quickly until the frequency shift was detected. After repeating several times in this way, a complete curve of frequency shift was obtained.

The sensors were tested with two kinds of procedures: humidity ascending (HA-mode) and descending (HD-mode) process. HA-mode and HD-mode were carried out individually to analyze the humidity sensing properties.

In HA-mode, the sensor was placed in the testing room from humidity 11.28% to 83.62%. The frequency shifts of piezoelectric crystal in different humidity were detected. In HD-mode, the testing process was reversed.

3. Results and discussion

3.1. Microstructure characteristics of composite films

Fig. 3a–c are the scanning electron microscopy (SEM) images of different sensitive materials coated on the surface of QCM electrode. Fig. 3a describes the SEM image of UFR. The UFR are evenly distributed and connect closely on the surface of QCM electrode. The strongly hydrophilic groups of —NH_2 and —OH on the UFR can absorb the water molecules. The nano silica particles (Fig. 3b) are well scattered on the surface of QCM electrode. Small voids and openings occur between the particles that are much looser than those of the UFR. Water molecules can penetrate the voids and openings easily to combine with the Si—OH of the silica via hydrogen bonding. However, simple nano-silica film is broken off easily from the surface of QCM electrode. Once the incorporation UFR with nano-silica composite films (Fig. 3c) are deposited on the surface of QCM electrode, nano-silica particles are well dispersed in UFR matrix. Two types of sensitive materials can provide synergistic effects in the adsorption of water molecules.

3.2. The linearity of the humidity sensor

The mass ratio of urea and formaldehyde to nano-silica was fixed in Table 1. Fig. 4(a–f) are the response curves of frequency shift in different humidity with different mass ratio of urea and formaldehyde to nano-silica. Fig. 4a illustrates the frequency shift