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ScienceDirect
Talanta 73 (2007) 857–861
Talanta
www.elsevier.com/locate/talanta

In situ prepared polypyrrole for low humidity QCM sensor and related theoretical calculation

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Received 13 March 2007; received in revised form 1 May 2007; accepted 1 May 2007
Available online 10 May 2007

Abstract

In situ preparation of polypyrrole (Ppy) by photo-polymerization coated on a quartz crystal microbalance (QCM) as a low humidity sensor was reported. Different concentrations of Ppy films say 0 wt.% (as blank), 0.1, 1, and 10 wt.% were investigated to measure humidity concentrations between 14.7 and 5412.5 ppm_v. The adsorption/desorption behavior was also examined at humidity concentration 510.2 ppm_v. The sensitivities of 0, 0.1 and 1 wt.% Ppy films at 51.5 ppm_v were 0.143, 0.219 and 0.427, respectively. For 1 wt.% Ppy, the highest sensitivity was obtained. The slope and correlation coefficients (R^2) for 1 wt.% Ppy at the ranges of 14.7–898.6 ppm_v were 0.0646 and 0.9909, respectively. A series of molecular simulations have been carried out to calculate bond energy for the water molecule interaction with Ppy, which was found to be ∼3 kcal/mol indicating the existence of hydrogen bonding during the sorption process. Based on Langmuir isotherm adsorption assumption, for 0.1 and 1 wt.% Ppy films, the association constants were 2606.30 and 5792.98, respectively. This larger association constant for 1 wt.% Ppy film explains higher sensitivity.

Keywords: Low humidity sensor; Polypyrrole; QCM; Photo-polymerization; Association constant

1. Introduction

Humidity is one of the most commonly measured physical quantities, significant to a wide variety of fields, like environmental, food and agriculture, industrial, clinical and biotechnological fields. In many specialty industries, nowadays low humidity detection becoming mandatory. Whilst measuring low humidity levels, often there has been great amount of confusion about the accuracy in humidity measurement. Notably, several promising technologies has been developed and applied to revolutionize the design of the accurate humidity sensors. However, it still remains demanding to develop a humidity sensor with complete set of characteristics, like, good linearity, high sensitivity, low hysteresis, rapid response time and obviously with low cost. Of the various sensing technologies for humidity detection, a majority are capacitive hygrometers, a conductive layer covered with an organic substance/polymer and a metallic layer thin enough to be porous to water vapor.

The quartz crystal microbalance (QCM) is an extremely sensitive mass sensor in the nanogram scale. The QCM detectors have also been used for a long time to monitor low humidity with wide measuring range contributing to several advantages [1–4]. The quantitative relationship between changes of frequency Δf (Hz) of piezoelectric crystal and the mass change caused by mass loading on the piezoelectric crystal surface have firstly derived by Sauerbrey [5]:

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

where f_o (MHz) is the basic frequency of the unloaded piezoelectric crystal, A (cm^2) the surface area of the electrode, and Δm (g) is the change in mass on the surface of the crystal.

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0039-9140/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.talanta.2007.05.002

Different sensing materials, such as modified nitrated polystyrene [6], TiO_2 nanowires/PAMPS [7], Nafion-Ag [8], MWCNTs/Nafion [9], SWCNTs/Nafion [10] and polypyrrole [11] were developed as films and are coated on the QCM electrode to detect vapor and humidity. Conducting polymers and their composites were extensively studied for the past two decades for applications like optical electronics [12], solar cell [13,14] and other sensing fields [15–17]. In recent years they have emerged as new type of smart materials for humidity sensing. Several sensors using conducting polymer materials were reported in the literature [11,18–21]. QCM sensors coated with conducting polypyrrole as sensing material for measuring humidity with relative humidity range [11], and hydrogen bonding was mentioned in humidity sensing by Collins and Buckley [19].

In this paper, we prepared Ppy coated over QC electrodes by photo-polymerization instead of complicated synthesis methods, and applied for low humidity sensing between 14.7 and 5412.5 ppm_v. Materials Studio® Version 3.2 (http://www.accelrys.com/products/mstudio/, Accelrys Software Inc.) was used for series of molecular simulations to calculate bond energy, towards water molecule adsorption to the Ppy surface, the bond distance between oxygen and hydrogen was calculated as 2.305 Å and the bond energy is around 3 kcal/mol that attribute to the presence of hydrogen bonding in the sorption process. At lower water vapor concentration, sensitivites are higher and the sorption behaviors were also calculated by the Langmuir isotherm adsorption conditions [8].

2. Experimental

2.1. Material preparation

All the chemicals used are analytical reagent (AR) grade (purity > 99%), purchased from Sigma–Aldrich Co., Inc., USA, unless otherwise mentioned. All the chemicals were used as received. Water was distilled and deionized (DI) using a 'Milli-Q' water purification system (Millipore Corp.).

Different concentrations of 10, 1, 0.1 and 0 wt.% of pyrrole (C_4H_5N) in ethanol (EtOH, 95%) were prepared and to these concentrations of pyrrole in EtOH solution, a 10 mol% of silver nitrate ($AgNO_3$) was added as an electron acceptor during photo-polymerization. The mixtures were sonicated for less than a minute, until the added $AgNO_3$ was completely dissolved. No significant data was obtained for the 10 wt.% Ppy, as the crystal could not oscillate further due to overloading.

2.2. Electrode of QCM fabrication

Planar AT-cut quartz crystals (QC) of 5 mm in diameter with a fundamental resonance frequency of 9 MHz were obtained from Affinity New Technology Co. Ltd., Taiwan. The gold electrode of the QCM was rinsed with DI water and then thoroughly cleaned ultrasonically in acetone. After drying, both sides of the QCM electrode were coated with the mixture solution. Polypyrrole (PPy) was synthesized using a UV-irradiation method [22]. A sensing film was coated onto quartz piezoelectric crystals using a commercial spin coater. The films were left 15 h under UV light (365 nm) to allow polymerization to complete, resulting in slightly black coloured films. The uncoated quartz crystal was used to compare the sensitivity with that of the doubly coated quartz crystal. All experiments were performed at room temperature (23.0 ± 1.5) °C

2.3. Equipment

Quartz crystal microbalance (ANT Inc., Taiwan) used in this study was a modified version from P-Sensor 1000, equipped with an ultra-high frequency counter (custom designed and fabricated for CMS/ITRI, by Affinity New Technology Co. Ltd., Taiwan; Chang, et al., USPTO 6557416, 06th May 2003) for counting the pulse signals and a potentiostat (PE-1000; Model #AA7706061, Affinity New Technology Co. Ltd., Taiwan) and a Spin Coater (PM-490, SWIENCO, YEONG SHIN Co. LTD, Taiwan). A divided humidity generator was used as the principal facility for producing the test gases. Required water vapor concentration was obtained by adjusting the proportion of dry and humid air generated by the divided flow humidity generator. The lowest testing point is limited by the dryness of the gas. A low humidity hygrometer (HYGROCLIP IC-3, Rotronic Inc., USA) and a QCM sensor were connected to an outlet of the divided flow humidity generator. The low humidity hygrometer was used as the reference standard for calibrating the QCM sensor. The volume ratio of the moist air was adjusted according to the reading of the low humidity hygrometer traceable to the National Measurement Laboratory, Taiwan (NML) humidity laboratory. The volume ratio of the moist air was calculated by the following equation:

$$\mathrm{ppm_v} = \frac{V_v}{V} \times 10^6 \quad (2)$$

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

where V_v is the volume of water vapor, V the total volume, e the partial pressure of water vapor and P is the total pressure. The schematic sketch of the system was shown in Fig. 1. Bond energy was calculated using Materials Studio® Version 3.2 software (Accelrys Software Inc.) evaluating the adsorption behavior of water vapor and Ppy.

3. Results and discussion

3.1. Adsorption simulation studies

Molecular simulations were done for hydrogen bonding energy calculation towards water molecule bonding to the Ppy surface was investigated. The total potential energies of Ppy and water molecules adsorbed Ppy is denoted as Ut(Ppy) and Ut(Ppy + H_2O), respectively. The hydrogen bond energy is the difference of total potential energy to the combined sum of potential energies of Ppy and H_2O, depicted in the form of equation as Ut(Ppy + H_2O) − (Ut(Ppy) + Ut(H_2O)). Thus, calculated adsorption simulation results for 1–50 water molecules were shown in Fig. 2.