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Swelling Behavior in Solvent Vapor Sensing based on Quartz Crystal Microbalance (QCM) Coated Polyacrylonitrile (PAN) Nanofiber

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Abstract. Polyacrylonitrile (PAN) nanofiber deposited on quartz crystal microbalance (QCM) substrate as solvent vapor sensing has been successfully developed. The absorption and swelling behavior has been assumed to be responsible for sensing mechanism in vapor sensing. In this study, we aim to investigate the correlation between the swelling degree (polymer-solvent affinity) and the sensor response. The PAN nanofiber has been successfully deposited on QCM substrate with relatively homogenous nanofiber diameter about (260 ± 20) nm. The tests vapor solvent was included dimethylformamide (DMF), dimethylacetamide (DMAc), ethylene glycol (EG), toluene, ethanol, and distilled water. The results indicated that the sensor response for various vapor solvent clearly influences by its polymer-solvent affinity. The highest sensor response was achieved with DMF vapor due to its highest affinity with PAN polymer. The swelling behavior of polymer can be a potential candidate for developing vapor sensors with a polymer as an active layer.

Keywords. PAN nanofiber, QCM, vapor sensing, swelling, polymer-solvent affinity.

1. Introduction

Recently, various vapor sensors have been developed by using different sensing materials, such as conducting polymers [1], inorganic thin films [2, 3], and semiconductor metal oxides [4, 5] with good results. Moreover, various vapor sensor was also have been developed based on different sensing mechanisms such as resistance sensor [6], photoelectric sensors [7], optical sensor [8], amperometric sensor [9] and acoustic wave sensor [9]. One of the kinds of acoustic wave (AW) sensor platform is quartz crystal microbalance (QCM). A QCM sensor operates based on acoustic-electric effect and mass deposition. A QCM sensor offers an accurate, convenient, and real-time detection, sensors with high sensitivity response that is widely used as vapor/gas sensors [10]. Nanostructure material especially nanofibers have received increasing attention for various applications including gas sensor application due to their large surface area, high porosity and interconnected porous structures [11,12].

Many researchers have been used electrospun nanofiber [13, 14] and polymer modified nanofiber [10, 15] as sensing layer for various vapor/gas sensing.

The sensing mechanism of vapor sensor mainly dominated by chemical interaction between the active layer and the analytes. However, many volatile organic compounds like methanol, ethanol, and toluene are not reactive at room temperature and mild conditions. Fortunately, they may have weak physical interactions with the sensing layer, involving absorbing or swelling the polymer matrices. These interactions do not vary the oxidation levels of conducting polymers, yet can also affect the properties of the sensing materials and make these gases/vapor detectable [16]. Several studies have been done investigating the swelling behavior of various polar solvent at electrospun nanofiber membrane in order to improve their electrical or mechanical properties [17–19]. The previous study conducted by Huang [17] investigated the swelling effect of polyacrylonitrile (PAN) nanofiber after solvent vapor treatment with N,N-dimethyl formamide (DMF). The results confirmed that swelling behavior occurred when PAN nanofiber was exposure with DMF. The swelling behavior of PAN nanofiber and DMF vapor is expected due to their high polymer-solvent affinity.

Even though the swelling mechanism was believed to be one of the common mechanisms in gas sensing devices, the deep investigation of the process and its correlation was still limited. In this study, we investigate the dependence of PAN nanofiber vapor sensor with its swelling behavior in order to get a better understanding of sensing mechanism due to the swelling process of a polymer nanofiber. The affinity between polymer and solvent has been believed to be the causes of swelling solvent in polymer matrices [20]. The swelling ability of solvent and the polymer is convinced to depend on their affinity. Meanwhile, the affinity between polymer-solvent can be calculated by its relative energy density (RED) which is the ratio between solubility parameter distance (R_a) and the interaction radius ($R_o R_0$) of the polymer. Therefore, with that knowledge, we are investigating the correlation between the relative energy density (affinity) with the PAN nanofiber sensor under influence of various solvent vapor.

2. Materials and methods

Polyacrylonitrile (PAN) polymer with a molecular weight of 150000 from Sigma−Aldrich was used for the preparation of nanofiber sensor. Non-ionic surfactant Triton x-100 was purchased from Merck, Germany. The solvents used for vapor sensing included N,N-dimethyl formamide (DMF), dimethylacetamide (DMAc), ethylene glycol (EG), toluene, and ethanol all analytical grade were purchased from Merck, Germany. AT-Cut QCM sensor with the gold electrode and 10 MHz resonant frequency were purchased from Novaetech, Italy. All above materials used as received without any further purification.

Polyacrylonitrile (PAN) solution was prepared by dissolving 0.6 g polymer PAN into 10 mL DMF followed by mechanical stirring at 1000 rpm for 4 h at ambient temperature until a homogeneous solution was achieved. After PAN fully dissolved in DMF, a small amount (1 %) of non-ionic surfactant Triton X-100 was added to the solution. The non-ionic surfactant is added to lower the surface tension of the solution. Followed by mechanical stirring at 900 rpm for 30 min to fully dissolved the surfactant. The solution then transferred into 10 mL plastic syringes for electrospinning process. When the electrospinning process was performed, a DC voltage of 10 kV was applied, and the tip to collector distance was set as 15 cm. The collector used in the electrospinning process was metal plate covered with aluminum foil with crystal QCM put in the collector. The electrospinning process was carried out for 30 s, 60 s, and 90 s to get a suitable thickness nanofiber film. Finally, the nanofiber film was placed in the desiccator for 12 h to evaporates the residual solvent before further treatment. Scanning electron microscope (SEM) JEOL-JSM-6510 with auto fine coater JEOL JEC-3000FC was used for investigating the morphologies of electrospun nanofiber PAN.

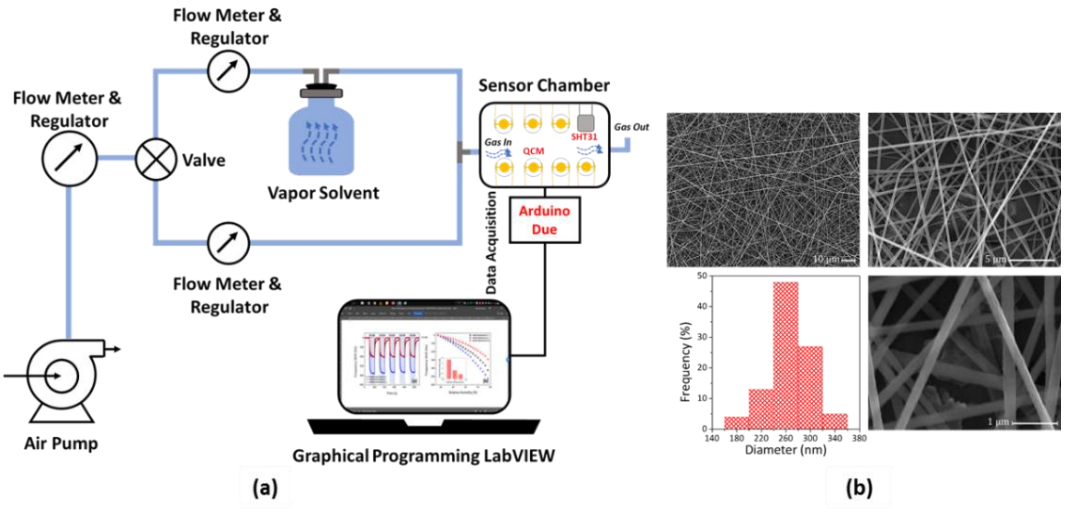

Figure 1. (a) Schematic illustration of PAN nanofiber QCM vapor sensing process, (b) SEM image of PAN nanofiber with different magnifications with nanofiber diameter distributions.

A schematic diagram of the solvent vapor sensing system is presented in Figure 1.a. The QCM sensor was installed in the testing chamber with Sensirion SHT 31 (temperature and humidity sensor) included to monitoring the humidity and the temperature of the chamber. During the experiments process, various of gas flow rate was used. The sensing of the QCM sensor was measured by a shift in the resonance frequency. The shift in the resonance frequency is directly related to mass deposition on sensing layer according to Sauerbrey equations. The resonance frequency sent to PC accompany RS232 or serial protocol with graphical programing language LabVIEW. To calculate the mass deposition of the PAN nanofiber, we used the frequency shift after coating based on Sauerbrey equations as follows [21].

$$\Delta f = -\frac{2 f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m \qquad (1)$$

where Δf represents the frequency shift of crystal QCM (Hz), f_0 is the intrinsic frequency (10 MHz), Δm is the mass variation (g), A is the electrode surface area (1.130 cm^2), and ρ_q and μ_q is the shear modulus and density of quartz crystal (2.947×10^{11} $g \cdot cm^{-1} \cdot s^{-2}$) and (2.648 $g \cdot cm^{-3}$), respectively.

3. Results and discussion

The PAN nanofiber vapor sensors deposited on quartz crystal microbalance (QCM) has been successfully performed. The smooth and continuous PAN nanofiber with relatively homogenous nanofiber diameter about 260 nm as shown in Figure 1.b. Nanostructured PAN nanofiber sensors offer large specific surface area, high porosity, and interconnected porous structures. As mention before that, the deposition time was varied to obtain different mass deposition. For convenience, we used the word QCM 1, QCM 2, and QCM 3 to refer the sample with deposition time 30 s, 60 s, and 90 s, respectively. The frequency shift after coating was increased for QCM 1 to QCM 3 and found about 530 Hz, 778 Hz, and 2163 Hz, respectively.

Figure 2.a shows the dynamic response of PAN nanofiber QCM sensors with various of vapor flow rate under the influence of N,N-dimethyl formamide (DMF) vapor against the background of ambient air ~ 50 % RH at room temperature. The frequency shift of the sensor shows increasing with the increase of the gas flow rate for all samples. The frequency of PAN nanofiber vapor sensor was decreased upon to increasing of vapor flow rate. Upon each injection of DMF vapor into the chamber, the sensor response showed a sharp drop and reached a steady value after several minutes. Figure 2.b shows the dynamic response (adsorption/desorption) of the sensor of PAN nanofiber sensors with 1

L/min vapor flow rate. The frequency shifts of the PAN nanofiber coated QCM sensor exposed to DMF vapor for 5 min were 12 Hz, 50 Hz, and 136 Hz for QCM 1, QCM 2, and QCM 3 respectively. The mass deposition of PAN nanofiber sensor shows in inset Figure 2.b and calculated by Sauerbrey equation in Equation 1. The mass deposition of PAN nanofiber vapor sensor was about 117 ng, 171 ng, and 476 ng for QCM 1, QCM 2, and QCM 3, respectively. The sensor response was increase with the increase of its mass deposition. Increasing mass deposition implies that the contact area between the active layer and the analysts was also increased, thus increasing the sensor response.

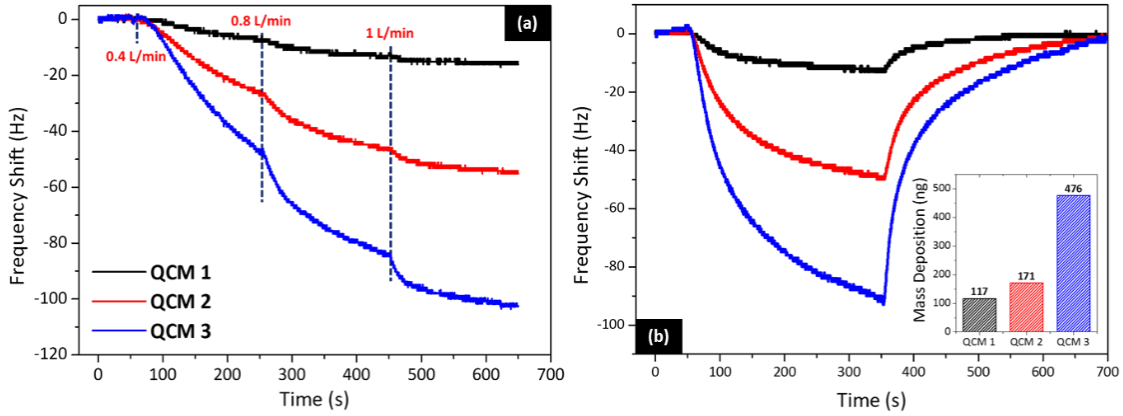

Figure 2. (a) Dynamic response of QCM sensors coated with PAN nanofiber upon exposure to increasing the vapor flow of dimethylformamide vapor, (b) One cycle of QCM response against DMF vapor (1 L/min) as a function of time for different PAN nanofiber samples (inset: mass deposition of PAN nanofiber sensors).

Figure. 3 shows the SEM image of PAN nanofiber before and after solvent evaporations. The results indicate there is a morphological change in PAN nanofiber film after evaporating with DMF vapor for one hour. The swelling behavior of PAN nanofiber under the influence of DMF vapor clearly seen at SEM images. When the PAN nanofiber film treated with DMF vapor, the film appeared to swell. This phenomenon is occurring because the vapor solvent can condense at nanofiber junction and slightly dissolved the polymer to facilitate fusion [17]. In addition to the swelling behavior, we also believe that another weak physical interaction (absorption) was also responsible for sensor response. Those two interactions occurred when PAN nanofiber under the influence of DMF vapor. The swelling behavior of PAN nanofiber under the influence of different solvent vapor is explained later.

The swelling phenomenon is commonly occurred to polymer due to absorption of solvent. The swelling degree of polymer-solvent depends on its affinity. The affinity of polymer-solvent normally express by their relative energy density (RED), which is the ratio between solubility parameter distance (R_a) and the interaction radius (R_o) of the polymer. The solubility parameter distance can be calculated with equation developed by Hansen and Skaarup in literature [20].

$$\left(R_a\right)^2 = 4\left(\delta_{Dp} + \delta_{Ds}\right)^2 + \left(\delta_{Pp} - \delta_{Ps}\right)^2 + \left(\delta_{Hp} - \delta_{Hs}\right)^2 \qquad (2)$$

where, δ_D is the density parameter of dispersion interaction, δ_P is density parameter of polar cohesive energy, and δ_H is density parameter of electron exchange parameter. Meanwhile, the interaction radius (R_o) of PAN is reported in the literature about 10.9 $MPa^{0.5}$ [20].

Table 1 shows the Hansen solubility parameter and the relative energy density value of the polymer and solvent used in this study. The relative energy density 0 means there is no energy difference, RED less than 1 indicate high affinity and RED greater than 1 indicate progressively lower affinity. The polymer-solvent affinity between PAN and the solvent progressively increased from distilled water,

EG, ethanol, methanol, toluene, dimethylacetamide, and dimethylformamide. The highest and the lowest affinity was possessed by DMF and distilled water, respectively.

Table 1. Relative Energy Density (RED), Hansen Solubility Parameters of polymer-solvent used in this study

Polymer/Solvent	Hansen Solubility Parameters [a]				$RED = \frac{R_a}{R_o}$
	δ_D	δ_P	δ_H	Δ_{total}	
Polyacrylonitrile (PAN)	21.7	14.1	9.1	27.4	–
N,N−Dimethyl formamide (DMF)	17.4	13.7	11.3	24.9	0.815
Dimethyl Acetamide (DMAc)	16.8	11.5	10.2	22.7	0.936
Toluene	18.0	1.4	2.0	18.2	1.498
Ethanol	15.8	8.8	19.4	26.52	1.517
Ethylene glycol (EG)	17.0	11.0	26.0	32.9	1.798
Distilled water	16.6	16.0	42.3	48.2	3.191

Figure 3.c shows the correlation between the response of the PAN sensor under the influence of different solvent versus its relative energy density. The higher response was achieved by the DMF vapor with 20 Hz frequency shift, while the lowest response with 2 Hz frequency shift was possessed by distilled water vapor. The results are indicating that response of the PAN nanofiber vapor sensor directly depended on their polymer-solvent affinity. The direct correlation between the PAN nanofiber sensor and their polymer solvent affinity is suitable for our main hypothesis.

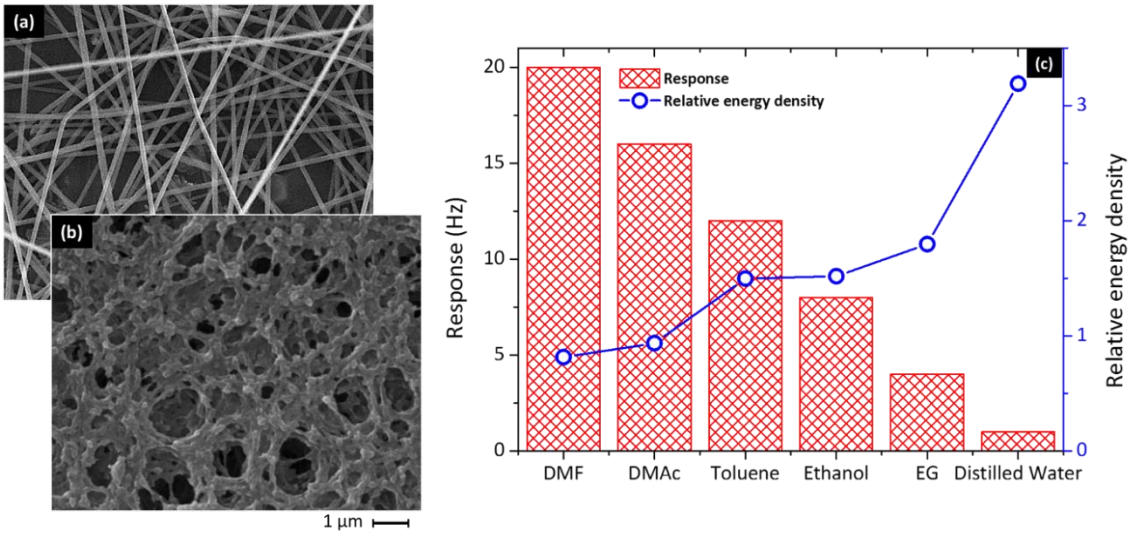

Figure 3. SEM image of PAN nanofiber sensor (a) before and (b) after vapor evaporation with DMF vapor for one hour; (c) PAN nanofiber response (QCM 1) under the influence of various solvent vapor with their relative energy density

4. Conclusions

This study has been successfully developed a vapor sensor based on PAN nanofiber deposits on QCM substrate. The PAN nanofiber structures were clearly seen by SEM images. The sensor also shows good sensitivity and medium response. The swelling behavior of PAN nanofiber under the influence of solvent vapor was evidenced by the SEM image. The swelling degree of between polymer and solvent depends on their affinity. The swelling mechanism has been confirmed to be responsible for

the response of the sensor; this could be an interesting approach to developed solvent vapor sensor devices.

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