Utilizing Bilayered Nano-porous ZnO Powder and PVC Composite Coating as the Sensing Film for Quartz Crystal Microbalance

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ABSTRACT

Nano-porous zinc oxide (ZnO) are used as the sensing material on quartz crystal microbalance (QCM) for volatile organic compounds (VOCs) detection. The Nano-porous ZnO powder were synthesized by co-precipitation and followed by firing process to control the porosity and morphology. The porous structure of ZnO powder provides high surface area for organic vapor adsorption and accessible channels for vapor diffusion. A thin layer of poly vinyl chloride (PVC) serves as the adhesion layer between ZnO and the gold of QCM electrodes. The rapid and reversible response signals suggest that sensing process involved only physical adsorption. Four volatile organic compounds with various functional groups were tested to demonstrate the selectivity differences between poly vinyl chloride (PVC) and porous ZnO powder. The finding in this work demonstrated that nano-porous ZnO powder can be used as a sensing material that can provide alternative selectivity and rapid response.

Keywords: quartz crystal microbalance, zinc oxide, poly vinyl chloride, volatile organic compounds

奈米孔氧化鋅及聚氯乙烯複合感測膜於石英晶體微天平之應用

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摘　　要

奈米孔氧化鋅被作為石英晶體微天平上的感測材料並應用於揮發性有機化合物之偵測。奈米孔氧化鋅藉由共沉澱進行合成並以燒結控制孔隙率及形貌。氧化鋅的多孔結構提供有機揮發性氣體吸附的高表面積及氣體擴散的適合通道。聚氯乙烯薄層在氧化鋅及石英微量天平的金電極表面之間充當黏著層。迅速可逆的反應訊號代表感測過程只涉及物理性吸附。本研究進行具有不同功能性官能基的四種揮發性有機化合物測試以顯示在聚氯乙烯及多孔性氧化鋅之間的選擇性差異。研究發現顯示奈米孔氧化鋅可以作為感測材料並且提供良好選擇性及迅速反應性。

關鍵詞：石英晶體微天平，氧化鋅，聚氯乙烯，揮發性有機化合物

文稿收件日期 105.11.16;文稿修正後接受日期 106.2.6; *通訊作者
Manuscript received November 16, 2016; revised February 6, 2017; * Corresponding author

I. INTRODUCTION

VOCs have always been an important category of hazardous pollutants [1]. It often presents as a mixture of various component due to the complexity of sources and their fate in the environment. The issue of this contaminant can be important in either indoor or outdoor environment [2]. Due to the diversity of chemical structure and different toxicity of individual compounds consisting VOCs, it is usually required to analyze the content of VOCs. Gas chromatograph equipped with mass spectrometry detector is by far the most reliable approach to tackle this challenge of analyzing VOCs in environment [3]. This method, however, requires sophisticate lab equipments and well trained personals to perform the analysis and to maintain the quality of working facilities. Therefore, the cost per measurement data is fairly high and it cannot be used as a continuous monitoring tool.

Chemical sensors provide an option of fast screening and monitoring choice for VOCs [4]. Earlier established VOC sensors such as tin oxide or other metal oxide sensor aim to respond to as many organic vapor as possible and serve as a total VOC indicator [5]. By incorporating the idea of sensor array, mixtures of VOCs can actually be recognized to a great extend [6]. It also has been show that unique selectivity of individual sensors among the array can greatly improve the capability of vapor identification. Throughout the past decades, selective responsive sensors based on nano-material coated chemiresistors or optical sensors have been developed [7, 8]. The concept of improving vapor recognition by employing hybrid array has also been reported [9].

Quartz crystal microbalance represents a convenient and yet unique platform for construction a chemical sensor. It is one of few devices that respond solely to the mass of surface adsorption when the sensing film is acoustically thin [10]. The frequency shift and the mass of sorption can be ascribed by well-know Sauerbrey equation [11]. A chemical sensor can be readily accomplished by coating a layer of sensing material on the surface of QCM. In the past decades, the performance of various coating material have been evaluated on QCM transducer. These sensing materials include: polymers or molecular imprinted polymer (MIP) [12, 13], Zeolites [14], macrocyclic ethers [15], monolayer-protected gold nanoclusters [16], carbon nanotubes [17, 18] and metal oxides [19-21]. QCM can not only use in gas phase but also for biological molecules detection in liquid phase [22]. Other specific application such as detection of dibutyl phthalate, a semi-volatile organic compound (SVOC), has also been reported [23].

In this work, we evaluate the selectivity of a new type of sensing material for QCM. ZnO with nano-pore structure were synthesized in batch and immobilized on QCM via a thin PVC interlayer. For the purpose of comparison, PVC coated QCM was tested together with ZnO coated QCM versus four organic vapors of different functional group. The sensing selectivity and mechanism were discussed.

II. EXPERIMENTAL SECTION

2.1 Synthesis of porous ZnO powder

Porous ZnO powder were prepared via the following procedures: An aqueous solution of 1.6 M $ZnSO_4$ was pumped into a 2 L glass reactor while continuously stirred. Simultaneously, a 2.0 M Na_2CO_3 solution and a 2.0 M NH_4HCO_3 solution, which was used as a chelating agent, were fed separately into the reactor. The pH and temperature were maintained at 7.0 and 60 ℃, respectively. After vigorous stirring for 20 hours, $ZnCO_3$ precipitations with particle diameters of approximately 10-50 μm formed. The carbonate particles were then fired at 950 ℃ for 12 hours to decompose the carbonate into porous ZnO powder. Synthetic process for other metal oxide with similar nano-porous structure can be found in a literature [24].

2.2 Preparation of QCM sensor

10 MHz At-cut QCM chips with gold plated electrodes were purchased from Taitien electronic Corp. (Taipei, Taiwan). The surfaces of gold electrodes were rinsed with deionized water and ethanol prior to coating. Polyvinylchloride (PVC) was obtained from Aldrich. The coating solution of PVC was prepared by merely dissolving PVC powder in

tetrahydrofuran at weight percentage concentration of 10%. The PVC film was then dip-coated on QCM and the frequency were recorded before and after film coating. A thin layer of PVC was used as the binder between ZnO and QCM surface. The reason of using PVC is due to its chemical inertness and ease of coating. PVC powder was dissolved in tetrahydrofuran (THF) to form a 5 % coating solution. The same dip-coating process was used for forming a thin PVC film on the surface of QCM. For the purpose of comparison, we retained some thin PVC-coated QCMs as the reference for ZnO-coated QCM responses. The powder-like ZnO was dispersed in another THF solution using both ultrasonic resonator and stir. A few μL of ZnO solution was drawn from the stirring solution and immediately dropped onto the PVC film on QCM surface. The THF associated with ZnO partially dissolved the PVC surface and allowing the ZnO powder to stick on the soften PVC surface. As the THF evaporated gradually, the PVC became harden again and the ZnO particles were immobilized on top of PVC film. The frequency shifts caused by PVC coating and ZnO coating after THF dried were recorded to account for the mass of coating layers.

2.3 Gas sensor test system

Fig.1 shows the diagram of vapor generation and gas sensor test system. Compressed air was passed through molecular sieve trap, activated carbon trap and HEPA to remove moisture, background organics and particles accordingly. The scrubbed air was divided and connected to three independent mass flow controllers. The first stream of air flow was directed into mixing chamber to control the dilution ratio of designated concentration. The second air flow was bubbled through a glass impinge, which was filled with 300 mL organic solvent to generate the vapor laden gas flow with saturated concentration. All organic solvents was purchased from either Alidrich (USA) or Fluka (Japan) with purity of 99% or higher. The first two streams of air flow joined at mixing chamber and the testing concentration was controlled by the flow ratio of these two flows. The third clean air flow was directly connected to the 3-way solenoid valves that allowed the flow direction to switch between test chamber and vent. The two solenoid valves were used to control whether the test vapor or clean air was delivered into test chamber.

QCM sensor was connected to home-made driving circuitry to produce an oscillating frequency near 10 MHz. The actual oscillating frequency was measured through a frequency counter (Agilent 5384A, Agilent, USA). The frequency counter was interfaced with computer via an IEEE488 (GPIB) to USB converter (National Instrument, Texas, USA). The frequency shifts during the course of experiment was recorded by computer using software written in LabWIEW (National Instruments).

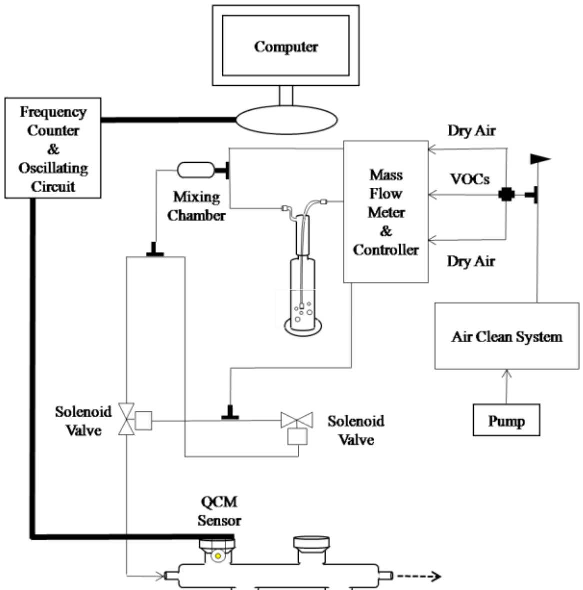

Fig.1. Schematic diagram of gas sensor measurement system

III. RESULTS AND DISCUSSION

3.1 Morphology of sensing material

The SEM images of PVC film and porous ZnO powder are shown in Fig. 2. Fig. 2a shows the image of a PVC film coated on a QCM. Fig. 2b reveals the detailed structure of ZnO powder. The porous structures formed after the ZnO particles being fired at 950^{o}C where $ZnCO_3$ was converted to ZnO. As it can be seen in this picture, the larger particle is formed by randomly stacking of nanoparticles to leave nano-pores and nano-channels on the surface of ZnO powder. The incomplete separation of nano-pores forms these nano-channels. These nano-pore and nano-channels can not only provide high surface area for vapor adsorption but also serve as the routes for gas diffusion in-and-out of ZnO particles.

The SEM images of ZnO sensing film on QCM using thin-PVC as binder are shown in Fig.2c and 2d. To ensure the sensor response are raised from ZnO mainly, the frequency shift due to PVC coating is 529 Hz which is relatively small comparing to that of ZnO coating (i.e., 12834 Hz). It is clear from these two images that ZnO powders are randomly attached on top of the PVC layer and ZnO particles do not fully cover the surface. Since the PVC adhesion layer is relatively thin, its contribution to sensor response can be considered as minor. However, when we evaluate this sensing film, the PVC adhesion layer and ZnO powder should be treated as a whole.

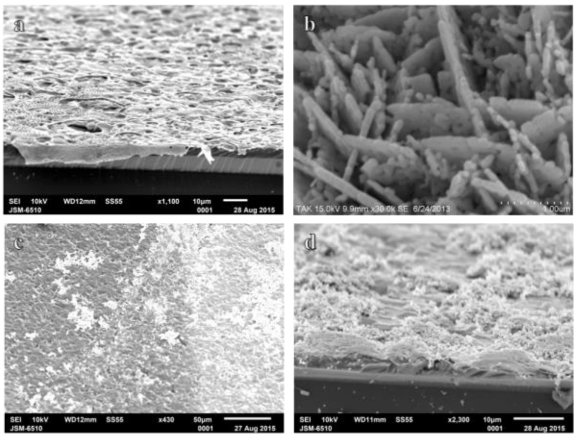

Fig.2. SEM images of (a) PVC film coated on QCM, (b) ZnO powders, and (c, d) ZnO/PVC film coated on QCM

3.2 Response signals of QCMs

Fig. 3 shows examples of QCM sensors responding to four organic vapors corresponding to six different concentrations. For the purpose of comparison, PVC was coated on another QCM at the mass loading of about 12000 Hz in frequency shift, which is similar to that of ZnO/PVC composite layer. The response signals of PVC-QCM to *m*-xylene, octane, butyl acetate and butanol are shown in the left part of Fig. 3 (3a,3c,3e and 3g). The response signals of ZnO/PVC-QCM to the same set of compounds are shown on the right of Fig. 3 (3b,3d,3f and 3h). Due to the stiff and dense nature of PVC polymer, slow responses and tailings were observed while vapors were adsorbed and desorbed from PVC film. It is also noteworthy that octane shows virtually no response on this sensor (Fig. 3c). In Fig. 3, it is clear that sensing capability were enhanced significantly with ZnO/PVC composite film on QCM. The response of all four tested vapors reached equilibrium relatively fast. The desorption after clear air apply had shown equal responding rate. The complete returning to the original baseline of QCM frequency before vapor exposure indicates the completeness of desorption. Therefore, there is no residual vapor on ZnO/PVC-QCM throughout the vapor sensing process.

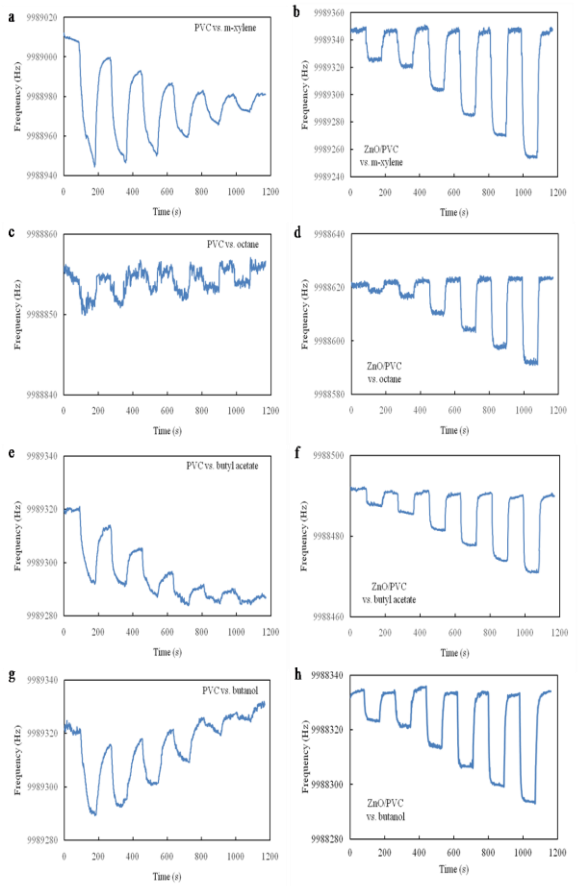

Fig.3. Response curves of PVC and ZnO/PVC coated QCM sensors at the various concentrations of (a, b) *m*-xylene, (c, d) octane, (e, f) butyl acetate, and (g, h) butanol

3.3 Calibration curves of QCMs

Since the QCM sensitivity is proportional to the thickness of the coating, it is often necessary to normalize the QCM response in respect to film thickness. A convenient approach divides vapor response (in Hz) with frequency shift (in Hz) and then times 100 for percentage (%) unit or 10^6 if the ppm unit were used. In Fig. 4, we use normalized responses in unit of ppm at y-axis so that it equivalent to the concentration unit (i.e., ppm) at x-axis. The thickness normalized calibration curves of PVC-QCM (Fig. 4a) and ZnO/PVC-QCM (Fig. 4b) for four tested VOCs are all in good linearity. Although m-xylene is the most sensitive compound for both PVC and ZnO/PVC coated QCM, the slopes for other three compounds are obviously different between two sensors. The slopes of calibration curves represents the sensitivity of a given vapor-sensor combination. The selectivity of PVC-QCM and ZnO/PVC-QCM are compared in following section.

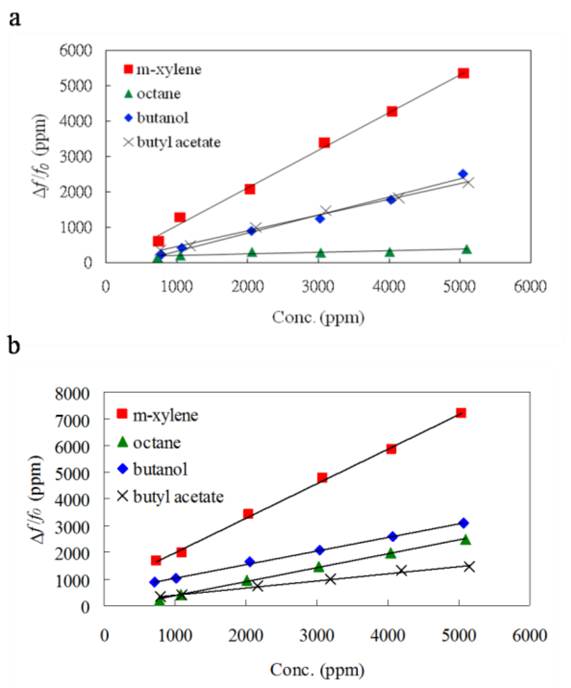

Fig.4. Calibration curves of four compounds tested with (a) PVC-coated and (b) ZnO/PVC-coated QCMs

3.4 Selectivity comparison

In order to compare their selectivity in detail, the relative sensitivities of two sensors versus four different vapors are plotted in Fig. 5. The height of each bar represents the sensitivity which is the slope of given QCM-vapor calibration curve from Fig. 4. As can be seen in Fig. 5, the selectivity for PVC-QCM is m-xylene > butanol ≒ butyl acetate >> octane. The selectivity for ZnO/PVC-QCM is m-xylene > octane ≒ butanol > butyl acetate. A significant difference response was found in octane sensing. PVC is a slightly polar polymer with dense structure. Octane was adsorbed poorly on the surface of PVC film. On the other hand, although ZnO is also in favorite of polar VOCs, its porosity provides high surface area for physical adsorption. Therefore, octane can still be adsorbed in the nano-pores of ZnO powder. This preliminary comparison demonstrated that ZnO powder did provide alternative vapor selectivity due to its surface chemical function that might be considered as a potential option for QCM coating selection.

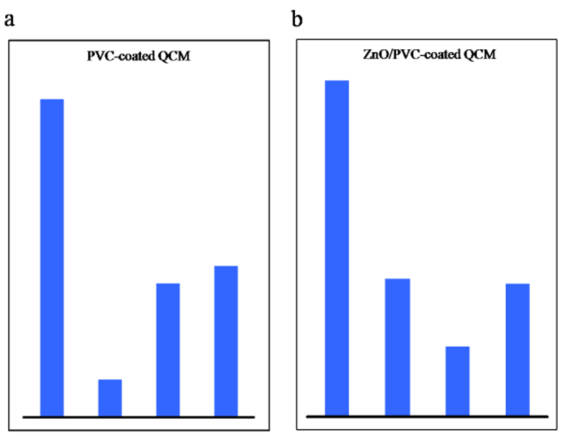

Fig.5. Response patterns of four compounds obtained from (a) PVC-coated and (b) ZnO/PVC-coated QCMs. Four compounds (from left to right)：*m*-xylene, octane, butyl acetate and butanol

3.5 Response mechanism

The rapid vapor sorption and desorption response curves indicated that only physical adsorption involved in the gas sensing process. The porous structures at nano-scale ensure there are additional surfaces for vapor adsorption inside the ZnO particles. Furthermore, the nano-pores and channels within the particles provide the route for fast mass transport. (Fig. 6) This is the reason why the response times appear to be shorter than polymer type QCM sensor.

The primary nano-ZnO particles that consists the porous structure are impenetrable. Therefore it relies solely on surface adsorption. The vapor response speed of ZnO/PVC-QCM shows significant improvement comparing to PVC-QCM.

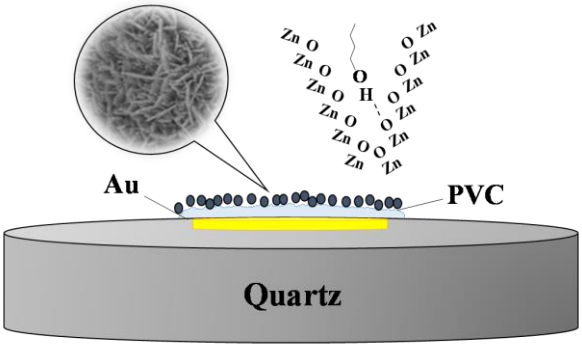

Fig.6. Adsorption models for ZnO with different volatile organic vapors

IV. CONCLUSIONS

This study investigates the potential usage of nano-porous ZnO powder as a sensing material for QCM transducer. The nano-porous structure of this material provides not only the higher surface area for adsorption of vapors but also the nano-voids for condensation at high concentration of vapors. Its porous nature can provide fast gas exchange without hysteresis. Also, ZnO is a very stable compound in atmosphere. Thus, ZnO coated QCM sensor is also durable.

REFERENCES

[1] Yu, C., and Crump, D., "A Review of the Emission of VOCs from Polymeric Materials Used in Buildings," Build. Environ., Vol. 33, pp. 357-374, 1998.
[2] Yang, S., Gao, K., and Yang, X., "Volatile Organic Compounds (VOCs) Formation due to Interactions between Ozone and Skin-Oiled Clothing: Measurements by Extraction-Analysis-Reaction Method," Build. Environ., Vol. 103, pp. 146-154, 2016.
[3] Wu, C. H., Feng, C. T., Lo, Y. S., Lin, T. Y., and Lo, J. G., "Determination of Volatile Organic Compounds in Workplace Air by Multisorbent Adsorption / Thermal Desorption - GC/MS," Chemosphere, Vol. 56, pp. 71-80, 2004.
[4] Singh, S., "Sensors - An Effective Approach for the Detection of Explosives," J. Hazard. Mater., Vol. 144, pp. 15-28, 2007.
[5] Sun, Y. F., Liu, S. B., Meng, F. L., Liu, J. Y., Jin, Z., Kong, L. T., and Liu, J. H., "Metal Oxide Nanostructures and Their Gas Sensing Properties: A Review," Sensors, Vol. 12, pp. 2610-2631, 2012.
[6] Hsieh, M. D., and Zellers, E. T., "Limits of Recognition for Simple Vapor Mixtures Determined with a Microsensor Array," Anal. Chem., Vol. 76, pp. 1885-1895, 2004.
[7] Yang, C. Y., Li, C. L., and Lu, C. J., "A Vapor Selectivity Study of Microsensor Arrays Employing Various Functionalized Ligand Protected Gold Nanoclusters," Anal. Chim. Acta, Vol. 565, pp. 17-26, 2006.
[8] Konvalina, G., and Haick, H., "Sensors for Breath Testing: From Nanomaterials to Comprehensive Disease Detection," Acc. Chem. Res., Vol. 47, pp. 66-76, 2014.
[9] Li, C. L., Chen, Y. F., Liu, M. H., and Lu, C. J., "Utilizing Diversified Properties of Monolayer Protected Gold Nano-Clusters to Construct a Hybrid Sensor Array for Organic Vapor Detection," Sens. Actuat. B: Chem., Vol. 169, pp. 349-359, 2012.
[10] Grate, J. W., and Zellers, E. T., "The Fractional Free Volume of the Sorbed Vapor in Modeling the Viscoelastic Contribution to Polymer-Coated Surface Acoustic Wave Vapor Sensor Responses," Anal. Chem., Vol. 72, pp. 2861-2868, 2000.
[11] Suaerbrey, G., "Verwendung von Schwingquarzen zur Wägung dünner Schichtenund zur Mikrowagung, Zeitschrift," Physik, Vol. 155, pp. 206-222, 1959.
[12] Öztürk, S., Kösemen, A., Sen, Z., Kılınç, N., and Harbeck, M., "Poly (3-Methyl-thiophene) Thin Films Deposited Electro-chemically on QCMs for the Sensing of Volatile Organic Compounds," Sensors, Vol. 16, pp. 423-434, 2016.
[13] Li, G., Zheng, J., Ma, X., Sun, Y., Fu, J., and Wu, G., "Development of QCM Trimethylamine Sensor Based on Water

Soluble Polyaniline," Sensors, Vol. 7, pp. 2378-2388, 2007.

[14] Kim, B. C., Yamamoto, T., and Kim, Y. H., "In-Line Measurement of Water Contents in Ethanol Using a Zeolite-Coated Quartz Crystal Microbalance," Sensors, Vol. 15, pp. 27273-27282, 2015.

[15] Lu, C. J., and Shih, J. S., "Detection of Polar Organic Vapours with Piezoelectric Crystals Coated with Crown Ethers," Anal. Chim. Acta, Vol. 306, pp. 129-137, 1995.

[16] Li, C. L., and Lu, C. J., "Establishing Linear Solvation Energy Relationships between VOCs and Monolayer-Protected Gold Nanoclusters Using Quartz Crystal Microbalance," Talanta, Vol. 79, pp. 851-855, 2009.

[17] Su, P. G., Sun, Y. L., and Lin, C. C., "A Low Humidity Sensor Made of Quartz Crystal Microbal-Ance Coated with Multi-Walled Carbon Nanotubes/Nafion Composite Materialfilms," Sens. Actuat. B Chem., Vol. 115, pp. 338-343, 2006.

[18] Lu, H. L., Lu, C. J., Tian, W. C., and Sheen, H. J., "A Vapor Response Mechanism Study of Surface-Modified Single-Walled Carbon Nanotubes Coated Chemiresistors and Quartz Crystal Microbalance Sensor Arrays," Talanta, Vol. 131, pp. 467-474, 2015.

[19] Zhang, K., Fan, G., Hu, R., and Li, G., "Enhanced Dibutyl Phthalate Sensing Performance of a Quartz Crystal Microbalance Coated with Au-Decorated ZnO Porous Microspheres," Sensors, Vol. 15, pp. 21153-21168, 2015.

[20] Xie, J., Wang, H., and Duan, M., "QCM Chemical Sensor Based on ZnO Colloid Spheres for the Alcohols," Sens. Actuat. B Chem., Vol. 203, pp. 239-244, 2014.

[21] Procek, M., Stolarczyk, A., Pustelny, T., and Maciak, E., "A Study of a QCM Sensor Based on TiO_2 Nanostructures for the Detection of NO_2 and Explosives Vapours in Air," Sensors, Vol. 15, pp. 9563-9581, 2015.

[22] Fuchiwaki, Y., Tanaka, M., Makita, Y., and Ooie, T., "New Approach to a Practical Quartz Crystal Microbalance Sensor Utilizing an Inkjet Printing System," Sensors, Vol. 14, pp. 20468-20479, 2014.

[23] Wang, Y., Ding, P., Hu, R., Zhang, J., Ma, X., Luo, Z., and Li, G., "A Dibutyl Phthalate Sensor Based on a Nanofiber Polyaniline Coated Quartz Crystal Monitor," Sensors, Vol. 13, pp. 3765-3775, 2013.

[24] Liu, M. H., Huang, H. T., Lin, C. M., Chen, J. M., and Liao, S. C., "Mg Gradient-Doped $LiNi_{0.5}Mn_{1.5}O_4$ as the Cathode Material for Li-Ion Batteries," Electrochim. Acta, Vol. 120, pp. 133-139, 2014.