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Development of a Quartz Crystal Microbalance Sensor Modified by Nano-Structured Polyaniline for Detecting the Plasticizer in Gaseous State

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Abstract: A quartz crystal microbalance (QCM) modified by a film of nano-structured polyaniline (nano-PANI) is developed as a gas sensor for detecting the presence of the plasticizer, such as dibutyl phthalate (DBP) in the ambient. Nano-PANI is prepared using a non-template method and the films are deposited using physical coating method. Scanning electron microscopy is used to characterize the nano-PANI film. The sensor response towards DBP is tested in a sealed gas chamber. The QCM resonant frequency shift is measured due to the absorption of DBP with different concentration ranging from 0.04 to 1.2 ppm. The experiment results show that the variation of the frequency is a linear function of DBP concentration and the sensitivity up to 54 Hz/ppm could be achieved by using the researched nano-PANI on QCM. To investigate the selectivity, the potential interfering analytes such as acetone, ethanol, acetaldehyde and formaldehyde are tested. And the mechanism hypothesis of the nano-PANI sensitive to the plasticizer is analyzed. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: Plasticizer, Dibutyl phthalate, Gas Sensor, Nano-structured Polyaniline, Quartz crystal microbalance.

1. Introduction

Plasticizers are additives that increase the plasticity or fluidity of a material. Dibutyl phthalate (DBP), one of phthalic acid esters, is widely used as additives to impart flexibility to polyvinyl plastics and other materials, including medical devices, pharmaceuticals, industry plastics, explosives, elastomers, safety glass, printing inks, paper coatings, and personal care products (e.g., perfumes, nail polishes and cosmetics) [1]. Toxicity studies have described that DBP exerts adverse effects on the development of the reproductive system of male rodent offspring, producing external and skeletal malformations through an antiandrogenic mechanism [2], following maternal oral intake [3, 4] or exposure [5, 6] throughout pregnancy, lactation and adolescence [7]. Moreover, some study showed a rapid skin penetration and systemic uptake of DBP in humans [8]. Health Canada has reported tolerable daily intake (TDI) of 0.0625 mg kg^{-1} day^{-1} for DBP [9], and the US Environment Protection Agency reported the reference dose (RfD) of 0.1 mg kg^{-1} day^{-1} for DBP in 1987 [10].

A quartz crystal microbalance (QCM) is extremely sensitive to mass change, which is extensively employed in gas analysis since King first introduced in 1964 [11]. The mass of the film (m) can be monitored by measuring the oscillating frequency change (Δf) of a quartz crystal and using the well-known Sauerbrey equation [12]:

$$\Delta f = -\frac{2 f_0^2}{A \rho_q \upsilon_q} \Delta m, \quad (1)$$

where Δf is the observed frequency change (Hz), f_0 is the fundamental resonant frequency of the crystal, A is the active area of the crystal (between electrodes), ρ_q is the density of quartz (2.649 g/cm^3) and υ_q is the shear wave velocity (2.947× 10^{10} N/m^2) in the quartz [13]. Recently, the electrodes of QCM coated sensitive films (e.g., polymer or copolymers [14], gold colloid [15], phthalocyanine [16] and pure n-alkanes [17]) were developed for determination of chlorinated aliphatic hydrocarbons [13], toluene [14], ethanol and methylamine [15], nitric oxide [16], ammonia [18], N_2 and Ar adsorption isotherms [19].

Polyaniline (PANI) has attracted much attention because of its environmental stability and its high electrical conductivity. In addition, it remains distinct from other polymers by possessing unique structural characteristics and the consequent redox behavior, interlinked with the degree of doping and protonation [13].

Although several QCM sensors coated by polyaniline have been successfully employed for the determination of gases [13, 20], DBP gas sensors based on coated QCM have seldom been investigated. We studied a QCM sensor with nano-structured polyaniline film for highly sensitive DBP detection in the air. Moreover, evaluation of the sensor performance, such as sensitivity, repeatability, selectivity and lifetime, has been done.

2. Experiment

2.1. Materials

Aniline (CAS No.: 62533, AR), ammonium peroxydisulfate (CAS No.: 7727540, AR), cetrimonium bromide (CAS No.: 57090, AR) and hydrochloric acid (CAS No.: 7647010, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aniline was freshly distilled in vacuum prior to use. Ethanol (CAS No.: 64175, AR), acetaldehyde (CAS No.: 75070, AR), acetone (CAS No.: 67641, AR) and formaldehyde solution (CAS No.: 50000, 37 % in H_2O, AR) were also all commercially available. AT-cut 6.0 MHz (HC-49/U) quartz crystals with silver electrodes on both sides were purchased from Hosonic International (Hangzhou) Ltd., China. The crystals were rinsed in 0.1 mol/L ethanol and then in deionized water prior to use. Deionized filtered water was used in all experiments.

2.2. Preparation of the QCM Sensor Based on the Nano-PANI Film

The coating mixture was prepared by adding equimolar aniline, ammonium peroxydisulfate and a small amount of cetrimonium bromide in a hydrochloride solution. The blue–black solution of polyaniline in water was obtained after standing for 24 h. Then certain volume (e.g. 10 microliters) of polyaniline aqueous solution were dispensed onto the surface of the electrode using a micropipette. The sensing film area was 0.5 cm^2. The device was dried in a dry cabinet at room temperature. Then a QCM sensor modified with a nano-structured polyaniline (nano-PANI) film was obtained.

2.3. Gas Sensing Experiments

The sensors were characterized in a 500 mL sealed chamber either in a high-purity N_2 or analytic gases at room temperature (15 degree Celsius). The analytic gases used during the investigation were DBP, ethanol, acetone, acetaldehyde and formaldehyde. An uncoated crystal was used as a reference QCM, while a nano-PANI film coated crystal was used as a sensing QCM. The frequency difference between sensing and reference QCMs was measured continuously with 1 second intervals. When an analytic gas was injected into the testing chamber, the frequency difference change was defined as the response of the sensor. When the QCM sensor response was stable, the high-purity N_2 purged the chamber to recover the sensor.

3. Results and Discussion

3.1. Scanning Electron Microscopy of the Nano-PANI Film

Scanning electron microscopy (SEM) observation was performed using a Field-Emission Scanning Electron Microscope with Energy Dispersive Spectrometer (FESEM-EDS, HITACHI S4800, Japan), operated at 5.0 kV. The nano-PANI film on the QCM sensor was deposited by platinum on the surface for SEM observation. Fig. 1 shows the surface morphology of the nano-PANI film, which is porous and consists of nanowires with wide diameter variations approximately from 20 nm to 100 nm. Disordered nanowires illustrate the textural framework of the nano-PANI film and such porous framework would be ideal for gas sensing, because it enhances the diffusion of target analytes inside the three-dimensional sensing matrix.

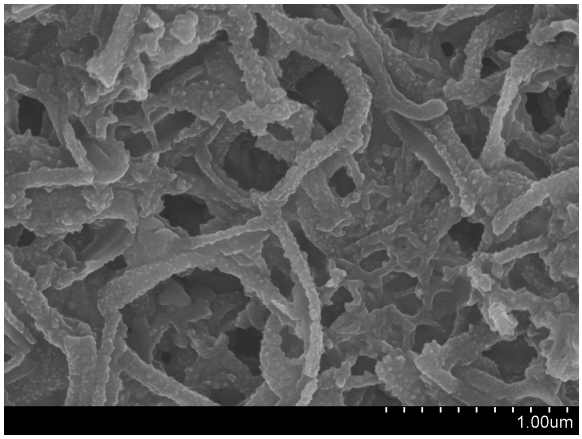

Fig. 1. SEM image of the nano-PANI film on a quartz crystal electrode.

3.2. Optimization of the Thickness of the Nano-PANI Film

The thickness of the nano-PANI film on the electrode should be considered as an important factor affecting the sensitivity of the gas sensor. The polyaniline film thickness was measured by a measuring microscope (107JA precise measuring microscope purchased from Shanghai CSOIF, Co., LTD., Shanghai, China). Fig. 2 shows the responses of the sensors to 0.2 ppm DBP, according to the thickness of the sensing films. As the thickness of polyaniline films increased from 4 to 20 μm, the responses increased obviously. When the thickness of polyaniline films was more than 20 μm, the responses did not increase dramatically further. In order to maintain the fastest response, the optimal thickness of polyaniline films of 20 μm was chosen.

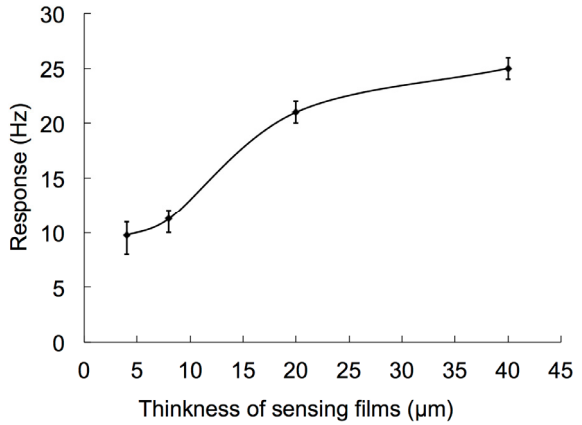

Fig. 2. Responses of QCM gas sensors to 0.2 ppm DBP with different thicknesses of nano-PANI films.

3.3. Sensitivity and Repeatability of the QCM Gas Sensor

Sauerbrey equation $\Delta f = -\frac{2f_0^2}{A\rho_q \upsilon_q}\Delta m$ gives the relationship between the change in the oscillation frequency of piezoelectric quartz (Δf) and the mass (Δm) added to the crystal.

When an analyte was injected into the testing chamber, the compound molecule was absorbed into the sensing film. The mass of the film on the QCM was increased and the sensing QCM's frequency decreased. The response increased, which was defined as the change of the frequency difference between the sensing QCM and the reference QCM. The sensor could be recovered by purging high-purity N_2 to desorb the gas molecules from the PANI film. Fig. 3 demonstrates the response cycles of a nano-PANI based QCM gas sensor to 0.2, 0.4, 0.6 and 0.8 ppm DBP and purged by high purity N_2 at room temperature (15 degree Celsius). The gas sensor had a good repeatability for every DBP concentration and the response time (t_{90}) was less than 30 seconds. It can be seen in Fig. 3 that the sensors could be recovered by high-purity N_2 purgation easily.

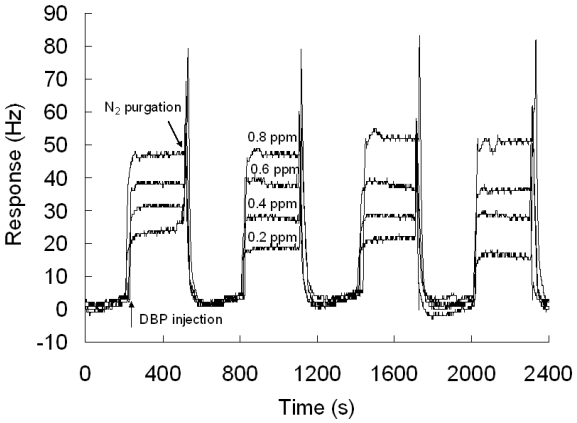

Fig. 3. Frequency cycles of the QCM gas sensor coated by the nano-PANI film response to different concentrations of DBP and purged by high-purity N_2 at room temperature.

The calibration curve of the nano-PANI based QCM sensor is shown in Fig. 4. The sensors were tested with a purging step in N_2 for 5 minutes and a sensing step in DBP of gas state for 5 minutes alternately. Each response (R) of the sensor to DBP concentration (C) was repeatedly measured 4 times. As shown in the Fig. 4, responses of the sensor were almost linear proportional to the DBP concentration in the range from 0.04 to 1.20 ppm. The regression equation is $R = 53.6\,C + 3.7$ with a correlation coefficient of 0.998. The limit of detection (calculated as three times the signal-to-noise ratio) was 0.02 ppm.

3.4. Selectivity

In order to investigate the selectivity of nano-PANI film based QCM gas sensor, the frequency changes of the sensor response to acetone, ethanol, acetaldehyde and DBP were measured. The sensors'

responses to acetone, ethanol, acetaldehyde and formaldehyde were still far less than to DBP, though the concentration of the contrast analyte (20 ppm) was 25 times higher than that of the target analyte DBP (0.8 ppm). The frequency difference is shown in Fig. 5. This experiment illustrated that the sensor had an excellent selectivity to DBP from acetone, ethanol, acetaldehyde and formaldehyde, though they have similar molecular structures to some extent.

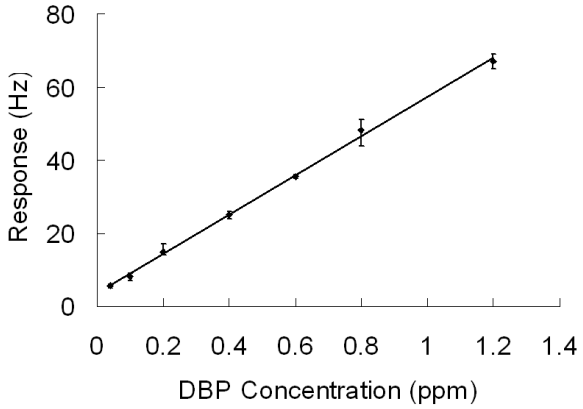

Fig. 4. Calibration curve of the nano-PANI film based QCM sensor response to DBP.

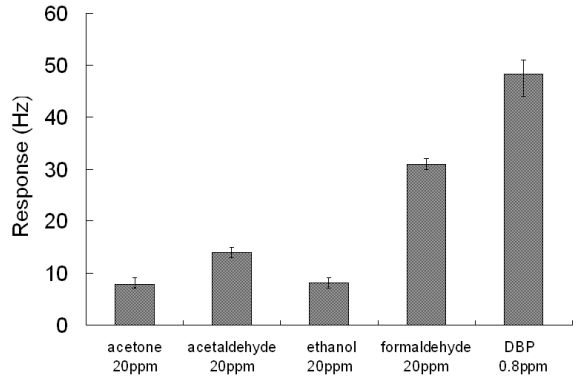

Fig. 5. The selectivity of the nano-PANI based QCM gas sensor (the concentration of acetone, ethanol, acetaldehyde and formaldehyde was 20 ppm and the concentration of DBP was 0.8 ppm).

3.5. Long-Term Stability

To assess the long-term stability of the nano-PANI based QCM sensor, the frequency response cycles measured immediately after fabrication and in 20 days storage were recorded and compared. As seen in Fig. 6, it can be demonstrated that the response amplitude and recovery of the sensor remained almost unchanged, after stored in a dry cabinet at room temperature for 20 days.

3.6. Mechanism of the Nano-PANI Sensitive to DBP

The plasticizer acts on a polymer that has many points of attachment along the polymer chain by breaking the attachment at places and masking the centers of force (we need not define them yet as Van der Waals, London, Debye, hydrogen bonding, crystal, or primary valence forces) that have held these polymer chains together. The plasticizer masks these centers of force by selectively solvating the polymer chain at these points. There may be such a force between the hydrogens in –NH- group of polyaniline and the oxygens of the ester group or electron clouds of the benzene rings in DBP.

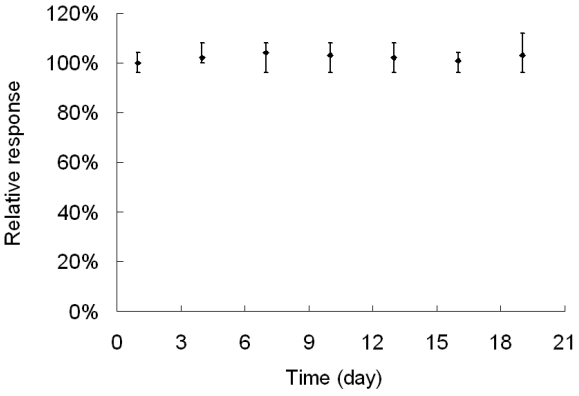

Fig. 6. The relative response of the sensors to 0.8 ppm DBP changes in 20-day storage in a dry cabinet at room temperature.

4. Conclusion

A simple non-template method was applied to prepare the nano-structured polyaniline. And a QCM gas sensor based on a nano-PANI film was developed to sense the plasticizer DBP in gaseous state. The satisfactory performance of the QCM sensor was obtained, such as the high sensitivity, the good selectivity and the long-term stability. This QCM gas sensor is simple-made and low-cost, that has potential to be commercial DBP-sensitive sensors for industrial and environmental applications.

Acknowledgements

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References

[1]. CIRC (Cosmetic Ingredient Review Committee), Final report on the safety assessment of dibutyl phthalate, dimethyl phthaiate, and diethyl phthalate, *Journal of the American College of Toxicology*, Vol. 4, 1985, pp. 267-303.

[2]. E. Mylchreest, R. C. Cattley, P. M. D. Foster, Male reproductive tract malformations in rats following gestational and lactational exposure to Di(n-butyl) phthalate: an antiandrogenic mechanism?, *Toxicological Sciences*, Vol. 43, Issue 1, 1998, pp. 47-60.

[3]. V. Salazar, C. Castillo, C. Ariznavarreta, R. Campón, J. A. F. Tresguerres, Effect of oral intake of dibutyl phthalate on reproductive parameters of Long Evans rats and pre-pubertal development of their offspring, *Toxicology*, Vol. 205, Issue 1-2, 2004, pp. 131-137.

[4]. M. Ema, E. Miyawaki, K. Kawashima, Effects of dibutyl phthalate on reproductive function in pregnant and pseudopregnant rats, *Reproductive Toxicology*, Vol. 14, Issue 1, 2000, pp. 13-19.

[5]. M. Ema, A. Harazono, E. Miyawaki, Y. Ogawa. Embryolethality following maternal exposure to dibutyl phthalate during early pregnancy in rats, *Bulletin of Environmental Contamination and Toxicology*, Vol. 58, Issue 4, 1997, pp. 636-643.

[6]. K. L. Howdeshell, J. Furr, C. R. Lambright, C. V. Rider, V. S. Wilson, L. E. Gray Jr. Cumulative effects of dibutyl phthalate and diethylhexyl phthalate on male rat reproductive tract development: altered fetal steroid hormones and genes, *Toxicological Sciences*, Vol. 99, Issue 1, 2007, pp. 190-202.

[7]. T. T. Higuchi, J. S. Palmer, J. L. Earl Gray, D. N. R. Veeramachaneni, Effects of dibutyl phthalate in male rabbits following in utero, adolescent, or postpubertal exposure, *Toxicological Sciences*, Vol. 72, Issue 2, 2003, pp. 301-313.

[8]. N. R. Janjua, G. K. Mortensen, A.-M. Andersson, B. Kongshoj, N. E. Skakkebaek, H. C. Wulf, Systemic uptake of diethyl phthalate, dibutyl phthalate, and butyl paraben following whole-body topical application and reproductive and thyroid hormone levels in humans, *Environmental Science & Technology*, Vol. 41, 2007, pp. 5564-5570.

[9]. Health Canada, ARCHIVED – Dibutyl Phthalate – PSL1 (http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lsp1/phthalate_dibutyl_phtalate/index-eng.php).

[10]. Integrated Risk Information System, Dibutyl phthalate (CASRN 84-74-2) (http://www.epa.gov/iris/subst/0038.htm).

[11]. W. H. King Jr., Piezoelectric sorption detector, *Analytical Chemistry*, Vol. 36, Issue 9, 1964, pp. 1735-1739.

[12]. G. Sauerbrey, The use of quartz oscillators for weighing thin layers and for microweighing, *Zeitschrift für Physik*, Vol. 155, Issue 2, 1959, pp. 206-222.

[13]. M. M. Ayad, G. El-Hefnawey, N. L. Torad, Quartz crystal microbalance sensor coated with polyaniline emeraldine base for determination of chlorinated aliphatic hydrocarbons, *Sensors and Actuators B: Chemical*, Vol. 134, Issue 2, 2008, pp. 887-894.

[14]. M. Matsuguchi, T. Uno, T. Aoki, M. Yoshida, Chemically modified copolymer coatings for mass-sensitive toluene vapor sensors, *Sensors and Actuators B: Chemical*, Vol. 131, Issue 2, 2008, pp. 652-659.

[15]. K. Shinbo, H. Furukawa, Y. Ohdaira, K. Kato, F. Kaneko, Hybrid gas sensing utilizing localized surface plasmons of gold colloid and a quartz crystal microbalance, *Thin Solid Film*, Vol. 516, Issue 24, 2008, pp. 9020-9024.

[16]. A. Palaniappan, S. Moochhala, F. E. H. Tay, X. Su, N. C. L. Phua, Phthalocyanine/silica hybrid films on QCM for enhanced nitric oxide sensing, *Sensors and Actuators B: Chemical*, Vol. 129, Issue 1, 2008, pp. 184-187.

[17]. M. Cassiède, J. Pauly, M. Milhet, M. Rivaletto, I. M. Marrucho, J. A. P. Coutinho, J.-L. Daridon, A quartz crystal microbalance technique to study wax crystallization in the presence of gas, *Measurement Science and Technology*, Vol. 19, No. 6, 2008, pp. 065704-065710.

[18]. V. Georgieva, N. Donkov, L. Spassov, P. Petkov, V. Gadjanova, Detection of NH_3 by quartz crystal microbalance coated with TiO_2, *Journal of Physics: Conference Series*, Vol. 113, 2008, pp. 012053-012057.

[19]. Y. Aoki, M. Hashizume, S. Onoue, T. Kunitake, Determination of surface area and porosity of small, nanometer-thick films by quartz crystal microbalance measurement of gas adsorption, *The Journal of Physical Chemistry B*, Vol. 112, No. 46, 2008, pp. 14578-14582.

[20]. M. M. Ayad, N. A. Salahuddin, A. K. Abou-Seif, M. O. Al-Ghayesh, pH sensor based on polyaniline and aniline-anthranilic acid copolymer films using quartz crystal microbalance and electronic absorption spectroscopy, *Polymers for Advanced Technologies*, Vol. 19, Issue 8, 2008, pp. 1142-1148.