Sensors and Actuators B 160 (2011) 724–729

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Selective detection of trace 1-butanol by QCM sensor coated with copolymer P(HEMA-*co*-MA)

Xiao Fan, Binyang Du*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 25 May 2011
Received in revised form 30 July 2011
Accepted 18 August 2011
Available online 25 August 2011

Keywords:
QCM
1-Butanol
Detection
Copolymer

ABSTRACT

A novel copolymer P(HEMA-*co*-MA) was successfully designed and synthesized for the fabrication of copolymer-coated QCM sensors to detect vapor of organic pollutant in air. The QCM results indicated that the P(HEMA-*co*-MA)-coated sensors exhibited high sensitivity, stability and selectivity for the detection of 1-butanol vapor in air over toluene, *p*-xylene and butyl acetate, which are usually produced in the coating process of films on the back of solar cell array. The lowest detection limit of 1-butanol can reach 72 ppm, which can result in the frequency shift of 4.0 Hz (ΔF_3) for the QCM sensor coated with 161 nm thick P(HEMA-*co*-MA) thin film. Furthermore, such P(HEMA-*co*-MA)-coated QCM sensor was reusable and can be reactivated by releasing the adsorbed vapor in vacuum. These P(HEMA-*co*-MA)-coated QCM sensor may have potential application in the monitoring and controlling the concentration of 1-butanol vapor in the factory of back-film producer of solar cell array, which may be helpful for the healthy of the related personnel in the production of solar cell array.

1. Introduction

In the last decade, the rapid economic growth has resulted in the serious natural environmental pollution. All kinds of environmental pollutants enter water, soil and atmosphere, which not only pollute the natural environment, but also harm the human survival and health. The volatile organic compounds (VOCs) are one kind of important source of pollutions in the air. The identification and monitoring of VOCs [1–5] have become serious tasks in many countries of the world, and are important for the early control of environmental pollution. Nowadays, solar energy is made use of more and more, and one of the most important applications is solar cell. However, the process of solar cell production will produce a variety of pollutants. For instance, various VOCs, which include toluene, *p*-xylene, butyl acetate and butanol, have been used in the coating process of films on the back of solar cell array.

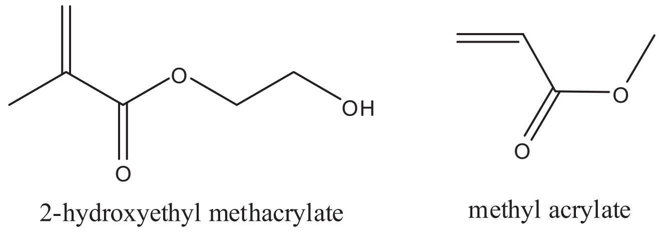
At present, there are many monitoring methods in the detection of VOCs, in which the most reliable and standard method for analyzing VOCs is the use of solid absorbent with post-analysis carried out in the laboratory [6], such as gas chromatography–mass spectrometry (GC–MS) and infrared spectroscopy. Though those methods have high sensitivity and selectivity, they require sample collection. What is more, off-site analysis is costly and time-intensive. In order to monitor VOCs effectively and selectivity, various synthetic films which have special affinity to certain VOCs are combined with proper real-time sensor (i.e. the quartz crystal microbalance or the surface acoustic wave device) [7–9]. This new attractive alternative can be placed in situ, reducing the requirement of grab samples and expensive off-site analysis. One of the widely-used devices is quartz crystal microbalance (QCM), which is a resonant sensor. The sensing film is coated on the surface of quartz crystal, of which an increase of mass due to absorption of the target molecules produces a shift of the crystal resonance frequency. QCM has high sensitivity, and can detect the trace mass changes in the nanogram range in air or liquid onto the electrode surface of quartz crystal. By making use of it, the monitoring of VOCs has enhanced sensitivity and is time saving because of real-time analysis.

Currently, the polymeric materials have been used to modify the surface of quartz crystal, which greatly enlarged the area of applications of QCM. There are many polymers that are widely chosen for detection of protein [10,11], heavy metal ions [12–14], organic gas [15–18] and organic compounds [19–21] by QCM. However, QCM sensors for detecting VOCs have to meet many challenges. How to enhance sensitivity, selectivity, shorten response time, stabilize reproducibility are still a subject for research. Fu and Finklea [15] reported the recognition of organic vapors in dry air based on molecularly imprinted polymers. They used hydroquinone and phenol as templates which generated shape-selective cavities in polymer matrix. The imprinted polymers exhibited high sensitivity and selectivity toward planar analytes. However, the cross-linked polymers were insoluble and needed adhesive for binding on the electrode surface of quartz crystal. Palaniappan et al.

---

* Corresponding author.
E-mail address: duby@zju.edu.cn (B. Du).

0925-4005/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2011.08.055



Scheme 1. The chemical structures of monomers, HEMA and MA.

[22] have enhanced the sensitivity of QCM sensors for gas detection by depositing a mesoporous silica film on the electrode surface. They used a sol–gel process in combination with plasma calcination, and β-cyclodextrin trapped in the mesoporous network to detect benzene and ethanol vapors. They demonstrated that the surface area of the silica controlled the sensitivity and the chemical property of β-cyclodextrin controlled the selectivity of the sensing system. The lowest detection limit of benzene can reach the concentration of 5 μL in 8 L chamber (about 157 ppm). Ju et al. [16] have developed a poly(β-cyclodextrin-*co*-maleic anhydride)-coated QCM sensor. They prepared polymer using β-cyclodextrin as monomer and maleic anhydride as crosslinker. They have studied the detection of benzene, toluene, and *p*-xylene in low concentrations. Linear calibrations were obtained for the three compounds with linear ranges of 400, 300, 150 ppm for benzene, toluene and *p*-xylene, respectively. Furthermore, *p*-xylene exhibited the highest sensitivity, which was 1.236 ± 1.994 Hz/ppm in average.

In the present work, we designed and synthesized a novel copolymer, which can be used as QCM coatings for highly sensitive and selective detection of 1-butanol. 1-Butanol is one of the key pollutants generated during the coating process of solar cell array. To our best knowledge, this is the first time to report a copolymer coated QCM sensor for the detection of 1-butanol in air. 1-Butanol has irritated and anesthesia effects on human body. When exposing to large dose of 1-butanol, the typical symptoms are the irritation of eyes, nose and throat, forming a semi-transparent bubble on the shallow surface of cornea, headache, giddiness and addiction in sleeping. If our hand comes into contact with large dose of 1-butanol, it will lead to skin inflammation [23–25]. According to the research of McCreery and Hunt [26], 1-butanol acts as a depressant of the central nervous system, which is similar to ethanol. Their study in rats indicated that the intoxicating potency of 1-butanol is about six times higher than that of ethanol, which possibly because of its slower transformation by alcohol dehydrogenase. Therefore, it is necessary and important to develop a sensing system, which can be used to monitor or detect the concentration of 1-butanol in the factory of back-film producer of solar cell array, in order to protect the healthy of personnel.

According to Hildebrand formula, if the solubility parameters of two molecules are similar, the enthalpy of mixing will be small. The solubility parameter of 1-butanol is 11.4. The solubility parameter of the copolymer poly(2-hydroxyethyl methacrylate-*co*-methyl acrylate) (P(HEMA-*co*-MA)) is 11.2, if the contents of 2-hydroxyethyl methacrylate (HEMA) and methyl acrylate (MA) in the copolymer were HEMA:MA = 1:1 (mol:mol) [27]. Due to this principle, 2-hydroxyethyl methacrylate (HEMA) and methyl acrylate (MA) were chosen as monomers. What is more, HEMA and MA contain oxygen atoms so that hydrogen bond may be formed between the copolymer and 1-butanol. The chemical structures of the two monomers were shown in Scheme 1. The copolymer, poly(2-hydroxyethyl methacrylate-*co*-methyl acrylate) (P(HEMA-*co*-MA)), was synthesized via free radical copolymerization. The copolymer-coated QCM sensors were fabricated by spin-coating of the copolymer solution onto the gold electrode surface of quartz crystal. These copolymer-coated quartz crystals were then used to detect trace toluene, *p*-xylene, butyl acetate and 1-butanol in air using QCM technique. The sensitivity and selectivity of the QCM sensors were systematically studied in response to the four vapors with various concentrations. It was found that the P(HEMA-*co*-MA)-coated sensor had higher selectivity and affinity to 1-butanol with detection limit of 72 ppm.

2. Experimental

2.1. Chemical and materials

2-Hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure. Methyl acrylate (MA), anhydrous tetrahydrofuran (THF; 99%, Sinopharm Chemical Reagent) and 1, 4-dioxane (99%, Sinopharm Chemical Reagent) were dried by refluxing in the presence of sodium flake and distilled prior use. The initiator, α,α′-azodiisobutyronitrile (AIBN) was recrystallized from methanol. All the other reagents were of analytical grade and used as received.

2.2. Synthesis of Copolymer P(HEMA-co-MA)

The copolymer, poly(2-hydroxyethyl methacrylate-*co*-methyl acrylate) (P(HEMA-*co*-MA)) was synthesized by free radical copolymerization of HEMA and MA using the Schlenk technique. Typically, 1 mL (8.25 mmol) of HEMA and 1 mL (11.08 mmol) of MA were dissolved in 20 mL of 1, 4-Dioxane with 10.0 mg of AIBN in a polymerization tube under magnetic stirring. Oxygen was eliminated by bubbling nitrogen through the solution for 30 min. The solution was then heated at 70 °C in an oil bath for 24 h under nitrogen bubbling. After the resulting reaction mixture was cooled down to room temperature, it was slowly added to 200 mL of frozen cyclohexane in a flask under stirring, and insoluble solid began to appear. 2 h later, the insoluble solid was first collected by vacuum filtration, and then washed by cyclohexane for several times. The white solid was dried overnight under vacuum at 50 °C, and then stored in desiccators for further uses.

2.3. Fabrication of copolymer thin films

The copolymer P(HEMA-*co*-MA) was dissolved in THF to give a series of solutions with different concentrations (0.5%, 1%, 1.5% and 2%). Polymer thin films were prepared by spin-coating. The solution was placed on one side of a clean quartz crystal with gold electrodes, and the crystal was spun at high speed (typically with 3000 rpm) to create a uniform polymer coating. The samples were then placed in vacuum for 24 h to remove the solvent. It was able to control the film thickness by changing the concentration of the solutions and the spin-coating speed.

2.4. Instrumental and characterization

The characterization of polymers was determined from FT-IR spectra and ^{1}H NMR. Vector 22 Bruker spectrometer was used for recording FT-IR spectra. ^{1}H NMR measurements of the polymers were performed on a 300 MHz Varian Mercury Plus NMR instrument with DMSO as solvent and tetramethylsilane (TMS) as internal standard. The molecular weights (include M_n and M_w) and molecular weight distribution of copolymer were determined using a gel permeation chromatograph (GPC, PL-GPC 220, Polymer Laboratories Ltd.) with tetrahydrofuran (THF) as the eluent and monodisperse polystyrene as the calibration standard.

The sensitivity, selectivity and stability of the copolymer-coated QCM sensors for the detection of trace volatile organic compounds in air were characterized using a quartz crystal microbalance (QTZ, Resonance Probe GmbH, Goslar, Germany). AT-cut quartz crystals (Maxtek, Torrance, CA) with a resonant frequency f_0 of 5 MHz and

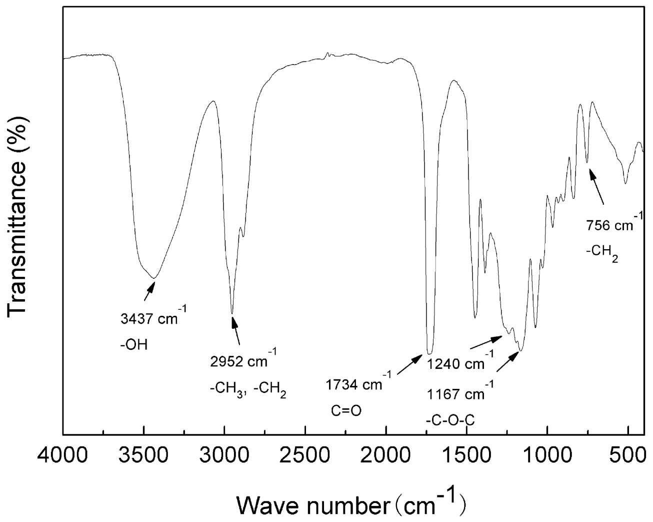


Fig. 1. FT-IR spectrum of the copolymer P(HEMA-*co*-MA).

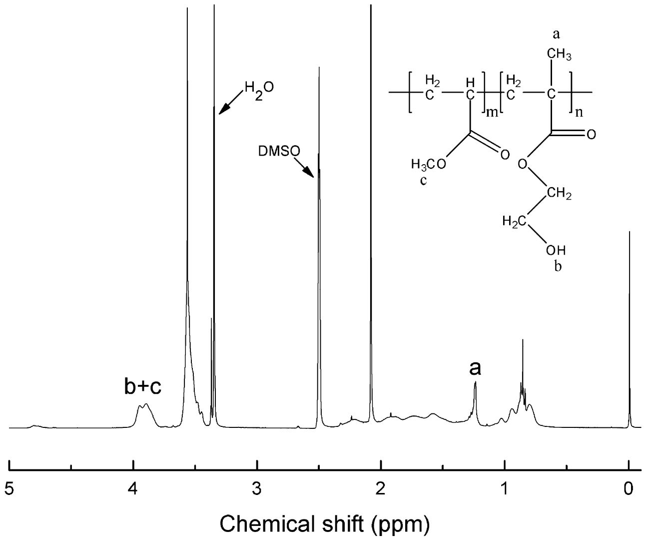


Fig. 2. ^{1}H NMR spectrum of the copolymer P(HEMA-*co*-MA).

gold electrodes were used. The quartz crystals were cleaned in piranha solution (the mixture of 30% H_2O_2 and 70% concentrated H_2SO_4) for 15 min, then flushed by de-ionized water and dried with nitrogen before measurement and spin-coating. (**Attention**! *Piranha solution is a very strong oxidizing agent. It should be handled with extreme care*.) Prior to the measurement, a clean quartz crystal was installed in the QCMs quartz holder, and the quartz holder was exposed in a gas chamber, which has a pinhole to inject gas or solvent. A stable baseline (±1 Hz/min) was first established for the bare quartz. After that, the quartz crystal was taken out and the copolymer film was fabricated on the crystal surface by spin-coating as mentioned above. The copolymer-coated quartz crystal was then put into the quartz holder again and the thickness of the copolymer thin film was determined by QCM in air according to the Sauerbrey equation. The QCM data were acquired at 3rd (15 MHz) overtone, and the frequency shift used throughout the text was ΔF_3. Till the baseline was stable for the copolymer-coated quartz crystal, a certain amount of volatile organic compounds was injected into the gas chamber through the pinhole by microliter syringe. The frequency shift of copolymer coated quartz crystal due to the adsorption of volatile organic compounds was recorded *vs* time. Typically, an adsorption *vs* time measurement lasted until equilibrium in adsorption was clearly reached. Afterward, another injection of testing VOC was performed. This process was repeated by several times, and a continuing adsorption curve was obtained. All experiments were conducted at room temperature of 25 °C.

The surface morphology of the copolymer thin films before and after adsorption of 1-butanol were also characterized by AFM (SPI3800N, Seiko Instrument Inc., Japan) operated in tapping mode at room temperature in air. Silicon tips (Olympus AC160TS, OLYMPUS BIOLAB, Japan) with a resonance frequency of ca. 300 kHz were used. Several different positions of each sample were imaged.

3. Results and discussion

3.1. Synthesis and characterization of copolymer P(HEMA-co-MA)

The copolymer P(HEMA-*co*-MA) was synthesized by free radical copolymerization of HEMA and MA as described in the experimental section and confirmed by the FTIR spectrum and ^{1}H NMR spectrum. Fig. 1 shows the FT-IR spectrum of P(HEMA-*co*-MA). The FT-IR spectrum clearly shows characteristic peaks of the copolymer, i.e. 3437 cm^{-1} (O–H stretching), 1734 cm^{-1} (C=O stretching), 1240 cm^{-1} and 1167 cm^{-1} (C–O–C stretching). Fig. 2 shows ^{1}H NMR spectrum of the copolymer P(HEMA-*co*-MA). All the peaks were appropriately assigned and indicated in Fig. 2. The contents of HEMA and MA in the copolymer P(HEMA-*co*-MA) were HEMA:MA = 1:1.1 (mol:mol) from the integral areas of peaks a and b + c. The FTIR and NMR results indicated the successful synthesis of copolymer P(HEMA-*co*-MA) and the copolymer was a random copolymer. The number-averaged molecular weight of P(HEMA-*co*-MA) was ca 3.6×10^4 with polydispersity of 2.80 as determined by GPC. As mentioned above, if the molar ratio of HEMA:MA is 1:1, the solubility parameter of the copolymer P(HEMA-*co*-MA) is 11.2. Since the molar ratio of HEMA:MA was 1:1.1 as revealed by ^{1}H NMR, the solubility parameter of the copolymer P(HEMA-*co*-MA) obtained here was thought to be close to 11.2. Note that the solubility parameter of 1-butanol is 11.4. Therefore, it was expected that the P(HEMA-*co*-MA) obtained here had higher affinity to 1-butanol.

3.2. P(HEMA-co-MA)-coated QCM sensors for detecting trace butanol in air

Copolymer P(HEMA-*co*-MA) thin films were then fabricated by spin-coating the copolymer THF solution onto the quartz crystals with gold electrodes. QCM was used to systematically study the sensitivity, selectivity, reproducibility and reusability of these copolymer-coated sensors in the detection of trace VOCs namely toluene, *p*-xylene, butyl acetate and 1-butanol, which are usually generated in the coating process of films on the back of solar cell array.

Fig. 3 shows the frequency shifts of the resonance frequency at 3rd overtone of the same P(HEMA-*co*-MA)-coated QCM sensor in response to various vapors of VOCs. It can be seen that the resonance frequency decreased when injecting the VOCs, indicating the absorption of the volatile VOCs onto the P(HEMA-*co*-MA)-coated QCM sensor. The toluene and *p*-xylene vapors led to irregular behavior of frequency shifts as increasing the concentration of vapors. These data suggest that the P(HEMA-*co*-MA)-coated QCM sensor is not suitable for the adsorption and sensing of toluene and *p*-xylene. For butyl acetate and 1-butanol, the frequency shift of P(HEMA-*co*-MA)-coated QCM sensor increase with increasing the concentration of vapors. With each injection step, the resonance frequency of the sensor decreases due to the continuous adsorption of butyl acetate or 1-butanol, as shown in Fig. 3c and d, respectively. In another word, the P(HEMA-*co*-MA)-coated QCM

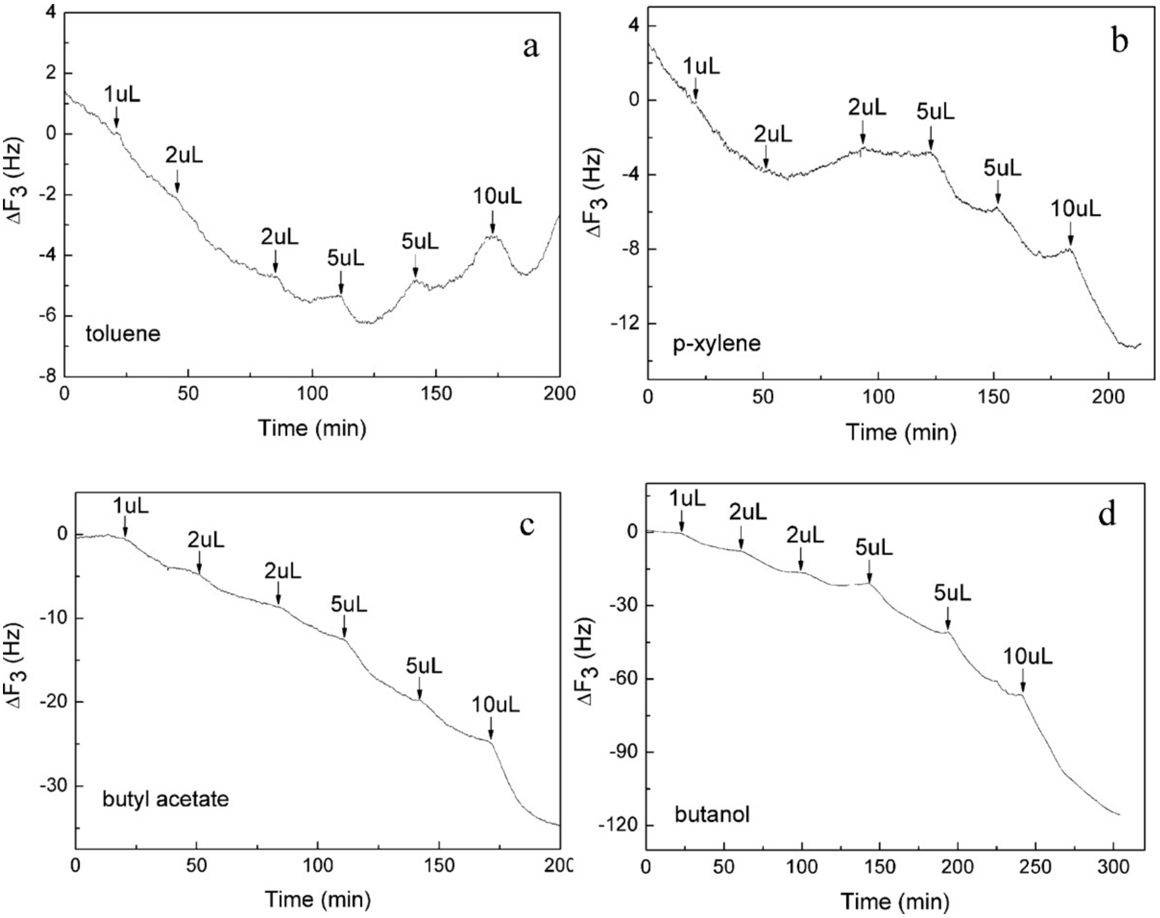


Fig. 3. The frequency shift of P(HEMA-*co*-MA)-coated QCM sensors in response to various kinds of VOCs: (a) toluene, (b) *p*-xylene, (c) butyl acetate, and (d) 1-butanol. The thickness of the P(HEMA-*co*-MA) thin film was 161 nm. The arrows in the figures indicated the amount of VOC injected into the testing chamber at each step.

sensor had higher frequency response for higher concentration of butyl acetate and 1-butanol vapor. These results indicate that the P(HEMA-*co*-MA)-coated QCM sensor is suitable for the sensing of butyl acetate and 1-butanol. Furthermore, it can be seen that the response of P(HEMA-*co*-MA)-coated QCM sensor to 1-butanol is much more significant than that to butyl acetate. It is also worthy to note that the P(HEMA-*co*-MA)-coated QCM sensor is reusable. After the vapor sorption measurement, the P(HEMA-*co*-MA)-coated QCM sensor can be reactivated by placing the sensor in vacuum for 24 h to release the adsorbed vapor. The reactivated sensor can be further used to detect the VOC vapor. Fig. 3d also indicates that frequency response of the sensor was reliable and stable adsorption equilibrium was achieved in response to the same amount of 1-butanol. Fig. 4 plots the frequency shift of P(HEMA-*co*-MA)-coated QCM sensor as a function of concentration of the four

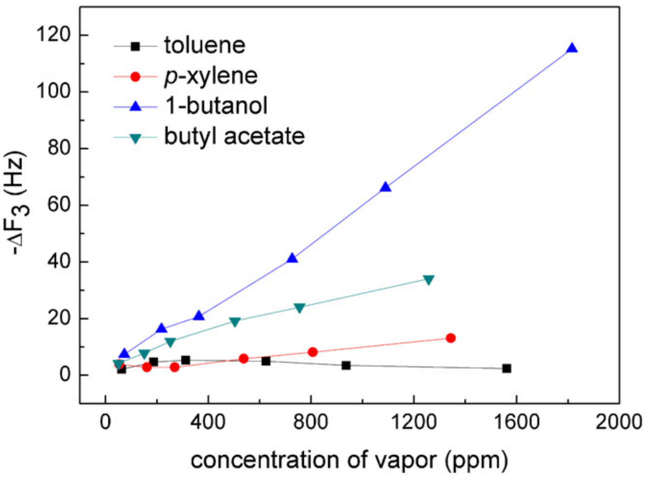


Fig. 4. The frequency shifts of the P(HEMA-*co*-MA)-coated QCM sensor in response to the vapors of toluene, *p*-xylene, butyl acetate, and 1-butanol with various concentrations.

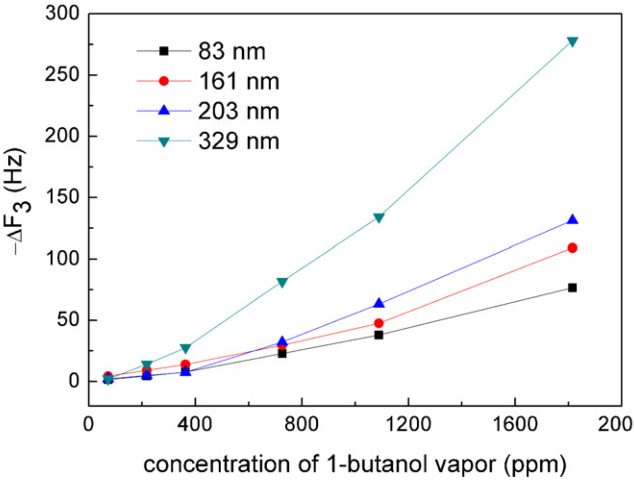


Fig. 5. The frequency shifts of the P(HEMA-*co*-MA)-coated QCM sensors with different film thicknesses in response to the vapor of 1-butanol.

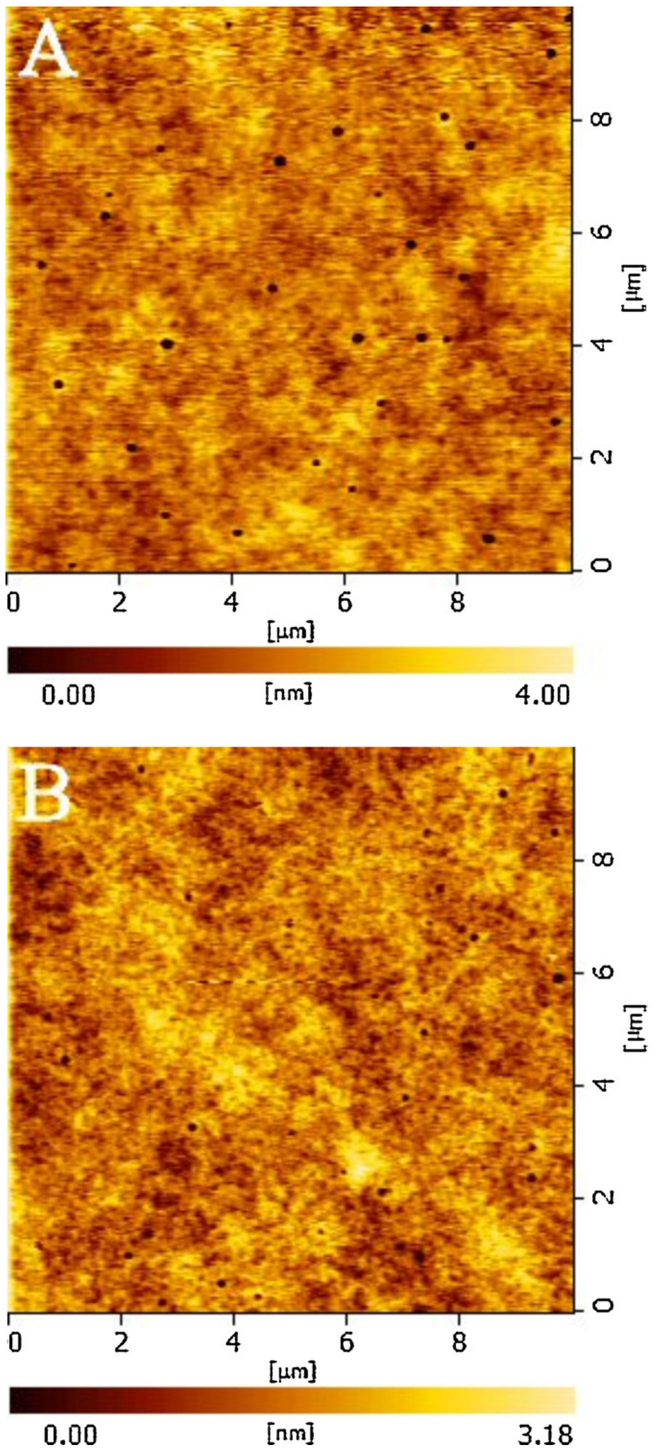


Fig. 6. AFM surface morphologies of P(HEMA-*co*-MA)-coated QCM sensor (A) before and (B) after the absorption of 1-butanol.

VOCs, i.e. toluene, *p*-xylene, butyl acetate, and 1-butanol. It can be clearly seen that the P(HEMA-*co*-MA)-coated QCM sensor exhibited the biggest affinity to the 1-butanol and absorbed 1-butanol vapor preferably. It was expectable since the solubility parameter of the copolymer P(HEMA-*co*-MA) obtained here was close to the of 1-butanol. These results showed that the P(HEMA-*co*-MA)-coated QCM sensors exhibited high selectivity for the detection of 1-butanol over toluene, *p*-xylene and butyl acetate.

The effect of film thickness on the frequency response of P(HEMA-*co*-MA)-coated QCM sensors to 1-butanol was further investigated. The thickness of P(HEMA-*co*-MA) thin films can be controlled by varying the concentration of copolymer and the spin-coating speed. Note that the film thickness was measured by QCM as described in experimental section. Fig. 5 shows that the frequency shifts of P(HEMA-*co*-MA)-coated QCM sensors with various film thicknesses in response to the various concentrations of 1-butanol. A general tendency can be observed that the frequency response of P(HEMA-*co*-MA)-coated QCM sensors to 1-butanol was enhanced with increasing the film thickness for the same concentration of 1-butanol vapor. For example, the frequency shift increases from ca. 76 Hz for 83 nm P(HEMA-*co*-MA) thin film up to ca. 278 Hz for 329 nm P(HEMA-*co*-MA) thin film in response to 1-butanol vapor of 1815 ppm. However, the frequency responses of the sensors with various film thicknesses to the low concentration of 1-butanol were slightly varied. The thicker film can possibly result in a decrease of sensing sensitivity for the P(HEMA-*co*-MA)-coated QCM sensors. It is understandable since the damping of quartz crystal increased with thicker coating, which will have less sensitive to the adsorption of small amount of vapor. The lowest detection limit of P(HEMA-*co*-MA)-coated QCM sensor for 1-butanol can reach as low as 72 ppm, which led to the frequency shift of 4.0 Hz (ΔF_3) for 161 nm thick P(HEMA-*co*-MA) thin film.

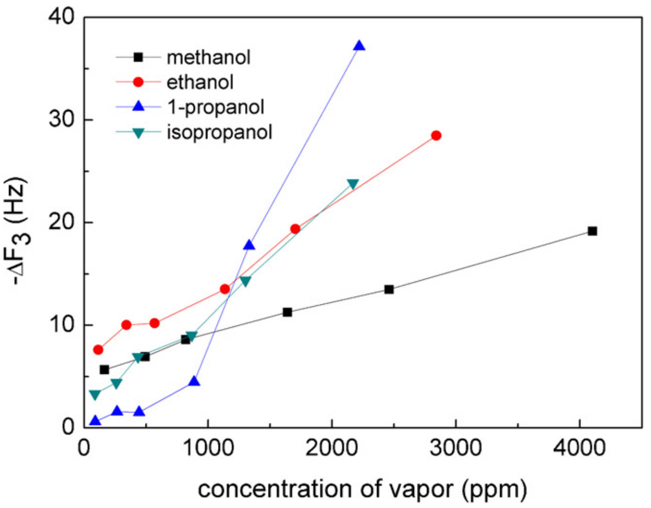


Fig. 7. The frequency shifts of the P(HEMA-*co*-MA)-coated QCM sensor in response to the vapors of methanol, ethanol, 1-propanol, and isopropanol with various concentrations.

The surface morphologies of the P(HEMA-*co*-MA)-coated QCM sensor before and after adsorption of 1-butanol were characterized using atomic force microscopy (AFM), as shown in Fig. 6. It can be seen that the surface morphology of P(HEMA-*co*-MA) thin film was not affected by the 1-butanol vapor. The root mean square (RMS) surface roughness of the copolymer film was similar before and after sensing measurement, i.e. 0.5 nm and 0.4 nm before and after adsorption of 1-butanol, respectively. These are very important for polymer-based QCM sensors. If the surface morphologies of polymer thin film were changed due to the VOC vapor, the sensors cannot be reused and the interpretation of the QCM data may be complicated.

The P(HEMA-*co*-MA)-coated QCM sensor was further tested in response to the vapors of other alcohols, i.e. methanol, ethanol, 1-propanol and isopropanol. The solubility parameters of methanol, ethanol, 1-propanol and isopropanol were 14.5, 12.9, 11.9, and 11.5, respectively. Fig. 7 plots the frequency shift ΔF_3 of P(HEMA-*co*-MA)-coated QCM sensor as a function of concentration of the four alcohols. The thickness of P(HEMA-*co*-MA) thin film was 169 nm as measured by QCM. It can be seen that the P(HEMA-*co*-MA)-coated QCM sensor does respond to different alcohols. As comparing with

Fig. 5, it is obvious that the sensor exhibits the biggest affinity to 1-butanol than other alcohols. In another word, the P(HEMA-*co*-MA)-coated QCM sensor is less sensitive to methanol, ethanol, 1-propanol and isopropanol. Although the solubility parameters of 1-propaol and isopropanol (i.e. 11.9 and 11.5) are closer to that of 1-butanol (i.e. 11.4), the P(HEMA-*co*-MA)-coated QCM sensor still exhibits favorable affinity to 1-butanol especially at higher concentration. These results suggest that the solubility parameter of the target organic vapor only serves as the starting point for the designation of copolymer. The exact mechanism of P(HEMA-*co*-MA)-coated QCM sensor for sensitive and selective detection of 1-butanol is still unclear. Many cooperative factors may result in the high selectivity and sensitivity of P(HEMA-*co*-MA)-coated QCM sensor toward the detecting target, 1-butanol.

4. Conclusions

A novel copolymer P(HEMA-*co*-MA) was successfully designed and synthesized for the fabrication of copolymer-coated QCM sensors to detect the trace 1-butanol vapor in air. The P(HEMA-*co*-MA)-coated QCM sensor exhibited high sensitivity, stability and selectivity for the detection of 1-butanol vapor in air over toluene, *p*-xylene and butyl acetate. The lowest detection limit of 1-butanol can reach 72 ppm for the QCM sensor coated with 161 nm thick P(HEMA-*co*-MA) thin film. Furthermore, such P(HEMA-*co*-MA)-coated QCM sensor was reusable and can be reactivated by releasing the adsorbed vapor in vacuum.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos. 20874087 and 21074114) and 863 project (No. 2009AA04Z125) for financial supports. The authors thank the reviewers for their constructive comments.

References

[1] B. Li, G. Sauve, M.C. Iovu, M. Jeffries-El, R. Zhang, J. Cooper, S. Santhanam, L. Schultz, J.C. Revelli, A.G. Kusne, T. Kowalewski, J.L. Snyder, L.E. Weiss, G.K. Fedder, R.D. McCullough, D.N. Lambeth, Volatile organic compound detection using nanostructured copolymers, Nano Lett. 6 (2006) 1598–1602.

[2] V. Dua, S.P. Surwade, S. Ammu, S.R. Agnihotra, S. Jain, K.E. Roberts, S. Park, R.S. Ruoff, S.K. Manohar, All-organic vapor sensor using inkjet-printed reduced graphene oxide, Angew. Chem. Int. Ed. 49 (2010) 2154–2157.

[3] M. Schlupp, T. Weil, A.J. Berresheim, U.M. Wiesler, J. Bargon, K. Mullen, Polyphenylene dendrimers as sensitive and selective sensor layers, Angew. Chem. Int. Ed. 40 (2001) 4011.

[4] X. Chen, S.G. Parker, G. Zou, W. Su, Q.J. Zhang, beta-Cyclodextrin-functionalized silver nanoparticles for the naked eye detection of aromatic isomers, ACS Nano 4 (2010) 6387–6394.

[5] A.P. Washe, S. Macho, G.A. Crespo, F.X. Rius, Potentiometric online detection of aromatic hydrocarbons in aqueous phase using carbon nanotube-based sensors, Anal. Chem. 82 (2010) 8106–8112.

[6] W.A. McClenny, K.D. Oliver, H.H. Jacumin, E.H. Daughtrey, Ambient level volatile organic compound (VOC) monitoring using solid adsorbents—recent US EPA studies, J. Environ. Monit. 4 (2002) 695–705.

[7] T. Akimoto, Y. Ikeshita, R. Terashima, I. Karube, Plasma-polymerized films providing selective affinity to the polarity of vaporized organic solvents, Thin Solid Films 518 (2009) 333–337.

[8] S. Kurosawa, H. Harigae, H. Aizawa, K. Terashima, H. Suzuki, Gas recognition films fabricated by microplasma technology, J. Photopolym. Sci. Technol. 19 (2006) 253–257.

[9] F. Wang, Y. Yang, T.M. Swager, Molecular recognition for high selectivity in carbon nanotube/polythiophene chemiresistors, Angew. Chem. Int. Ed. 47 (2008) 8394–8396.

[10] H. Furusawa, T. Ozeki, M. Morita, Y. Okahata, Added mass effect on immobilizations of proteins on a 27 MHz quartz crystal microbalance in aqueous solution, Anal. Chem. 81 (2009) 2268–2273.

[11] Y. Pei, H. Yu, Z. Pei, M. Theurer, C. Ammer, S. Andre, H.-J. Gabius, M. Yan, O. Ramstrom, Photoderivatized polymer thin films at quartz crystal microbalance surfaces: sensors for carbohydrate–protein interactions, Anal. Chem. 79 (2007) 6897–6902.

[12] S.C. Ng, X.C. Zhou, Z.K. Chen, P. Miao, H.S.O. Chan, S.F.Y. Li, P. Fu, Quartz crystal microbalance sensor deposited with Langmuir–Blodgett films of functionalized polythiophenes and application to heavy metal ions analysis, Langmuir 14 (1998) 1748–1752.

[13] S.-J. Liu, H.-G. Nie, J.-H. Jiang, G.-L. Shen, R.-Q. Yu, Electrochemical sensor for mercury(II) based on conformational switch mediated by interstrand cooperative coordination, Anal. Chem. 81 (2009) 5724–5730.

[14] Z. Zhu, Y. Su, J. Li, D. Li, J. Zhang, S. Song, Y. Zhao, G. Li, C. Fan, Highly sensitive electrochemical sensor for mercury(II) ions by using a mercury-specific oligonucleotide probe and gold nanoparticle-based amplification, Anal. Chem. 81 (2009) 7660–7666.

[15] Y. Fu, H.O. Finklea, Quartz crystal microbalance sensor for organic vapor detection based on molecularly imprinted polymers, Anal. Chem. 75 (2003) 5387–5393.

[16] J.-F. Ju, M.-J. Syu, H.-S. Teng, S.-K. Chou, Y.-S. Chang, Preparation and identification of [beta]-cyclodextrin polymer thin film for quartz crystal microbalance sensing of benzene, toluene, and p-xylene, Sens. Actuators B Chem. 132 (2008) 319–326.

[17] P. Si, J. Mortensen, A. Kornolov, J. Denborg, P.J. Moller, Polymer coated quartz crystal microbalance sensors for detection of volatile organic compounds in gas mixtures, Anal. Chim. Acta 597 (2007) 223–230.

[18] M. Matsuguchi, T. Uno, T. Aoki, M. Yoshida, Chemically modified copolymer coatings for mass-sensitive toluene vapor sensors, Sens. Actuators B Chem. 131 (2008) 652–659.

[19] K. Das, J. Penelle, V.M. Rotello, Selective picomolar detection of hexachlorobenzene in water using a quartz crystal microbalance coated with a molecularly imprinted polymer thin film, Langmuir 19 (2003) 3921–3925.

[20] M. Cerruti, J. Jaworski, D. Raorane, C. Zueger, J. Varadarajan, C. Carraro, S.W. Lee, R. Maboudian, A. Majumdar, Polymer-oligopeptide composite coating for selective detection of explosives in water, Anal. Chem. 81 (2009) 4192–4199.

[21] G. Giancane, M.R. Guascito, C. Malitesta, E. Mazzotta, R.A. Picca, L. Valli, QCM sensors for aqueous phenols based on active layers constituted by tetrapyrrolic macrocycle Langmuir films, J. Porphyrins Phthalocyanines 13 (2009) 1129–1139.

[22] A. Palaniappan, X. Li, F.E.H. Tay, J. Li, X.D. Su, Cyclodextrin functionalized mesoporous silica films on quartz crystal microbalance for enhanced gas sensing, Sens. Actuators B Chem. 119 (2006) 220–226.

[23] A.D. Winer, A note on the substrate specificity of horse liver alcohol dehydrogenase, Acta Chem. Scand. 12 (1958) 1695–1696.

[24] H. Theorell, R. Bonnichsen, Studies on liver alcohol dehydrogenase. 1. Equilibria and initial reaction velocities, Acta Chem. Scand. 5 (1951) 1105–1126.

[25] A.D. Merritt, G.M. Tomkins, Reversible oxidation of cyclic secondary alcohols by liver alcohol dehydrogenase, J. Biol. Chem. 234 (1959) 2778–2782.

[26] M.J. McCreery, W.A. Hunt, Physico-chemical correlates of alcohol intoxication, Neuropharmacology 17 (1978) 451–461.

[27] A.E. Hectepob, Handbook of Polymer Physics and Chemistry, vol. 1, China Petrochemical Press, 1984.

Biographies

Xiao Fan is currently a graduate student in Department of Polymer Science and Engineering, Zhejiang University, China. Her researches mainly focus on the development of QCM-based gas sensors.

Dr. Binyang Du is an associate professor in Department of Polymer Science and Engineering, Zhejiang University, China. Dr. Du got his PhD degree at Changchun Institute of Applied Chemistry, Chinese Academy of Science in February 2002. After 4-year guest-researches in German Universities, he joined Department of Polymer Science and Engineering, Zhejiang University in 2006. His researches mainly focus on the QCM-based chemical sensors, polymer hydrogels, and the solution behavior of amphiphilic block copolymers.