

Synthesis and Sensitive Properties of Poly-(bistriethylphosphine)-platinum-diethynylbenzene for Organic Vapor Detection

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ABSTRACT: Poly-(bistriethylphosphine)-platinum-diethynylbenzene (Pt-DEB) was synthesized by dehydrohalogenation reaction. X-ray photoelectron spectroscopy (XPS), FTIR, and ¹H-NMR spectra were used to identify the formation of Pt-DEB target material. Sensitive properties of Pt-DEB-based quartz crystal microbalance (QCM) sensor to various organic vapors such as trichloromethane, tetrahydrofuran, acetone, isopropyl alcohol, ethanol, and methanol have been studied. The results show that Pt-DEB has good reversibility, reproducibility, and linear sensitivity to organic vapors at room temperature. The

sensitivity of Pt-DEB (dissolved in CHCl₃) toward CHCl₃ is clearly higher than that toward other analytes, and a larger molecular weight of alcohol has a higher sensitivity response. The Pt-DEB-based QCM gas sensor shows low detection limits ranging from 1.0 to 3.56 ppm for the organic vapors and stable performance during a period of 30 days. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 562–567, 2010

Key words: synthesis; gas sensors; organic vapor; quartz crystal microbalance

INTRODUCTION

There is an increasing interest in the fabrication of gas sensors based on polymeric materials, mainly due to their specific properties such as deposition simplicity, low cost, room-temperature operations, and a wide choice of parameters to modulate the sensor selectivity to different chemical species.^{1,2} Conventionally, polymeric materials consist of C, H, N, O, S, Cl, Br elements, and occasionally P. Compared with coordination polymers, organometallic polymers have metal-to-carbon bonds. As a result, the incorporation of transition metallic element into a polymeric skeleton shows an effective way to afford novel polymeric materials with different properties from common carbon-based polymers. Among them, polyynes containing transi-

tion metals in main chain have been studied in many advanced applications, such as nonlinear optics (NLO) device³ and gas sensors.⁴

Especially, Pt-polyynes have been found to be suitable for sensor application as they exhibit variation in optical, electrical, or mass properties when they interact with certain chemicals. Caliendo et al. synthesized a Pt-polyynone, namely poly-[1, 4-dihexadecyloxy-2, 5-diethynylbenzene-bis (triphenylphosphine) platinum (II)] (Pt-P-HDOB), and spin-coated it on the surface of a SAW delay line device to realize a chemical sensor.^{5,6} The sensor has been exposed to different chemicals to measure for the chemical concentrations, and it showed high sensitivity and reproducibility to relative humidity and methanol vapors. Penza et al. have reported a comparison of gas sensing properties for three polyynone polymeric films tested as a SAW-type transducer.⁷ It was found out that the SAW gas response of Pt-polyynone polymer is higher than that of polyynone polymers for each examined gas concentration.

In this work, poly-(bistriethylphosphine)-platinum-diethynylbenzene (Pt-DEB) was synthesized and spin-coated on quartz crystal microbalance (QCM) for gas sensor applications. FTIR spectra and X-ray photoelectron spectroscopy (XPS) were used to reveal the extent of conjugation and the nature of the ending groups. A ¹H-nuclear magnetic

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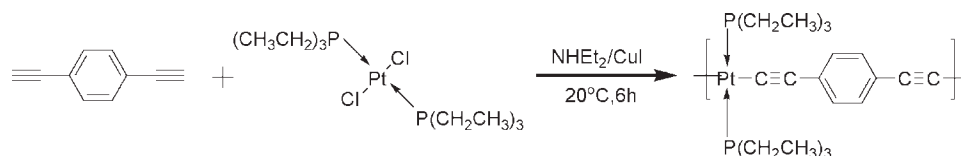


Figure 1 Schematic of Pt-DEB synthetic process.

resonance spectrum (¹H-NMR) was used to define the chemical and spatial structure of polymeric chains. Then, the obtained Pt-DEB was deposited on a QCM device to fabricate a sensor. The adsorption behavior and the sensitive properties to different organic vapors were evaluated. The sensitivity mechanism was also investigated.

EXPERIMENTAL

Pt-DEB synthesis and characterization method

Poly-(bistriethylphosphine)-platinum-diethynylbenzene (Pt-DEB) was synthesized according to common dehydrohalogenation reaction for the preparation of metal polyynes, which was performed by slight changing the procedure reported by Sonogashira.⁸ Trans-[Pt(nEt₃P)₂Cl₂] as precursor and 1,4-diethynyl benzene (DEB) as organic linker were purchased from Sigma-Aldrich. CuI as catalyst was purchased from Alfa Aesar and used as received. The schematic reaction procedure was shown in Figure 1.

Organic monomer 1,4-diethynyl benzene (0.135 g, 1.07 mmol) was dissolved in 50 mL of degassed diethylamine (NHEt₂) under N₂ circumstance, and 0.537 g (1.07 mmol) of trans-[Pt(nEt₃P)₂Cl₂] complex and 0.010 g (0.053 mmol) of CuI catalyst were added. The reactants were mechanically stirred at ambient temperature for 6 h. The product was then filtered off, washed with ethanol, and dried under vacuum.

FTIR spectrum was obtained using pellet samples of Pt-DEB powder mixed with KBr. The spectral region was from 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 4 cm⁻¹. An average of 25 scans was performed for each spectrum. The spectrum was characterized with a Nicolet MX-1E FTIR spectrometer. The chemical and electronic structure of organometallic polymer was investigated by XPS, which was carried out with a XSAM800 instrument with monochromatized Al K α radiation ($h\nu = 1486$ eV) at a pressure of 6.7×10^{-7} Pa. The spectra were energy referenced to the C_{1s} peak binding energy (BE) measured at 284.60 eV from Au 4f_{7/2} emission considered for the calibration of the spectrometer. ¹H-NMR spectra were recorded with a Bruker av 300 spectrometer at 300 MHz.

Fabrication of Pt-DEB based QCM gas sensor

For organic vapor sensitive test, QCM used in this study was 8 MHz AT-cut quartz crystal (silver sputtered electrode on titanium layer with a diameter of 4 mm on both sides). The Pt-DEB polymer film was spin-coated onto the surface of QCM device using trichloromethane (CHCl₃) as solvent. The film thickness is dependent on initial solution concentrations and the rates of spin coating. Residual solvent was removed by drying the devices in an oven at 60°C for several hours. The surface morphology of Pt-DEB film was characterized by a JSM-5900LV Scanning electron microscopy (SEM). The mass adsorbed on QCM device was inferred from the frequency shift measured with a frequency counter and calculated by Sauerbrey equation.⁹

$$\Delta f = -2.26 \times 10^{-6} f_0^2 \frac{\Delta m}{A}$$

where Δf is resonance frequency variation in hertz, f_0 stands for the resonance frequency of QCM as reference, A (cm²) is the effective area of electrodes, and Δm (g) is mass loading on crystal surface. The mass sensitivity of the QCM device is 1.74 ng/Hz.

Sensor measurement of organic vapors

The sensor measurement was carried out using a homemade detecting system.¹⁰ The QCM device coated with Pt-DEB film was suspended in a sealed glass vessel with a volume of 300 mL. Certain volume of liquid analyte was injected into the vessel by a microdispenser syringe and evaporated thoroughly at room temperature. The analyte was subsequently adsorbed onto the surface of Pt-DEB sensitive film, which induced the frequency of QCM device change. Then, the Pt-DEB-based QCM sensor was exposed to ambient air atmosphere to remove the analyte, and the frequency returned to the baseline between each measurement.

Here, trichloromethane, tetrahydrofuran, acetone, isopropyl alcohol, ethanol, and methanol were selected as analytes. Known volumes ranging from 2 to 10 μ L in a step of 2 μ L were injected in the test vessel, respectively. To unify the unit, we calculate organic vapor concentrations using ppm by the following equation, 1 ppm = 1 part in 10⁶ = 1

microlitre (μL) per liter (L).¹¹ As the total volume of the vessel used in our case is 300 mL, the earlier equation can be rewritten as follows: 1 ppm = 0.3 μL liquid organic vapor per 300 mL. The actual volumes injected were 2, 4, 6, 8, 10 μL , then the concentrations of organic vapors were 6.7, 13.3, 20, 26.7, 33.3 ppm, respectively.

QCM-5 Oscillator (Shenyang Vacuum Technology Institute) as described before¹⁰ excited the QCM device. The frequency shifts were monitored by a frequency counter (SS7200 intelligent counter, the Fourth Ratio Factory, China), which was connected to a computer system via a GPIB interface board and visualized by a SS7200 software program in a PC station for analysis. The signal measurements were carried out from frequency data collected at 1 point every 7 s.

RESULTS AND DISCUSSION

Characterization of organometallic polymer

As a comparison and aid for the assessment of polymer structure, the FTIR spectra of trans-[Pt(nEt_3P)₂Cl₂] complex and Pt-DEB polymer are shown in Figure 2. The upper figure is the FTIR spectrum of precursor, which is provided by Sigma-Aldrich. It is apparent that the organic moiety of Pt-DEB polymer is as same as trans-[Pt(nEt_3P)₂Cl₂] complex. However, in the FTIR spectrum of Pt-DEB, two characteristic bands at 2094.4 cm^{-1} ($\text{C}\equiv\text{C}$ stretching vibration) and 1592.9 cm^{-1} (weak, $\text{C}-\text{C}$ stretching vibration of the aromatic rings) can be found. Generally, $\text{C}\equiv\text{C}$ stretching vibration of disubstituted alkynes ($\text{RC}\equiv\text{CR}'$) occurs in 2260 cm^{-1} –2190 cm^{-1} (unconjugated). Conjugation with aromatic rings tends to slightly increase the intensity of $\text{C}\equiv\text{C}$ stretching vibration band and shift to a lower frequency of 2094.4 cm^{-1} .¹²

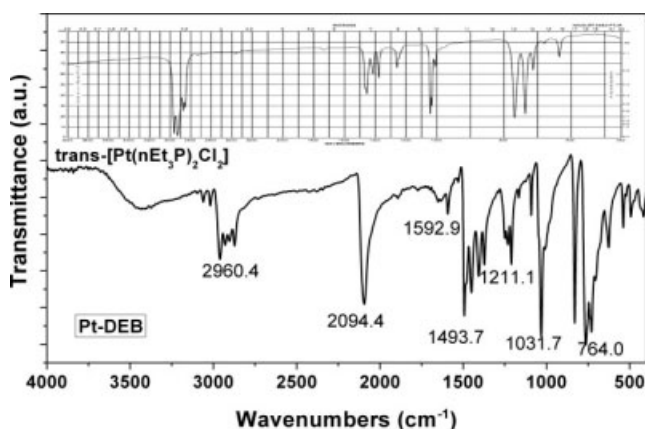


Figure 2 FTIR spectra of the trans-[Pt(nEt_3P)₂Cl₂] (provided by Sigma-Aldrich) and Pt-DEB.

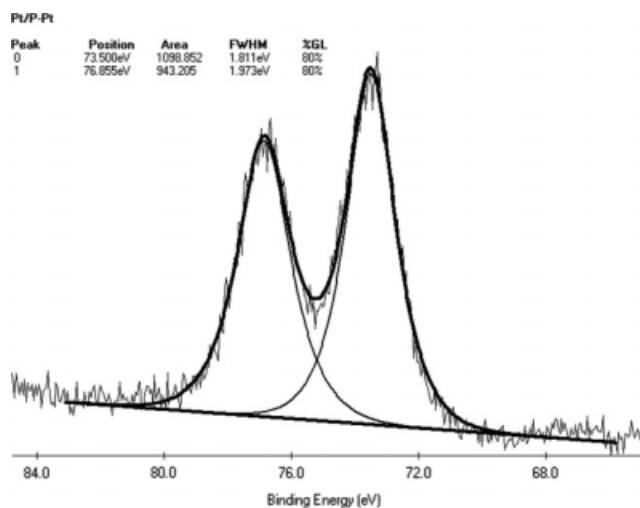


Figure 3 Pt $4f$ core level spectra of Pt-DEB.

The chemical and electronic structure of Pt-DEB polymer was further investigated by means of XPS. The Pt $4f$ core level spectrum in Pt-DEB is shown in Figure 3. The Pt $4f_{5/2,7/2}$ core level signals for Pt-DEB are found at 73.50 and 76.86 eV with a FWHM (full width at half-maximum) of 1.81 and 1.97 eV, respectively.

To verify the chemical structure, we also used $^1\text{H-NMR}$ spectra to characterize Pt-DEB in CDCl_3 solvent. $^1\text{H-NMR}$ data were found in the following order: chemical shift (ppm), spin multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and integration: 1.17 (m, 18H, $-\text{CH}_3$), 2.15 (m, 12H, $\text{P}-\text{CH}_2-$), 7.12 (s, 4H, Ar-H). The $^1\text{H-NMR}$ spectra is in good agreement with the chemical structure of Pt-DEB shown in Figure 1.

The surface morphology of materials is an important characteristic for the sensitive properties. The SEM image of Pt-DEB was shown in Figure 4. SEM operated at an electron voltage of 20 kV with a

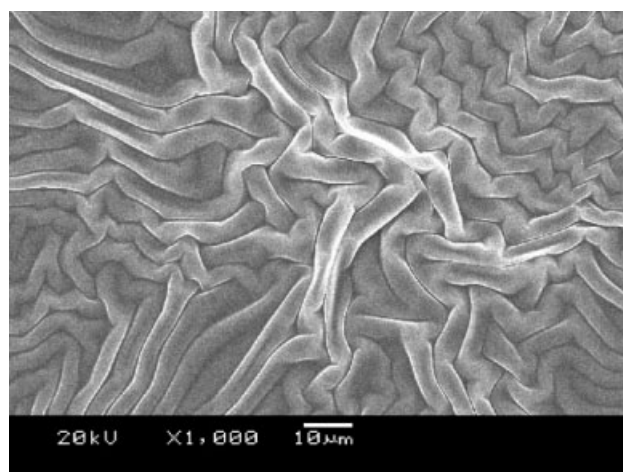


Figure 4 The SEM image of Pt-DEB film.

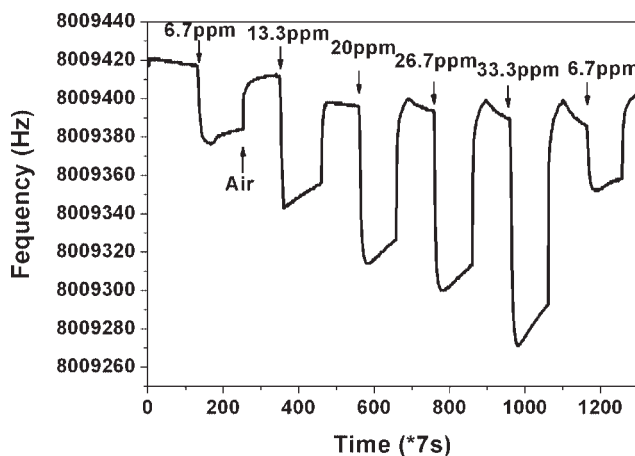


Figure 5 Real-time response of the Pt-DEB-based QCM sensor to trichloromethane.

magnification power of $1000\times$. Pt-DEB is soluble and makes film with a smooth and regular surface in ordered packing which is a good requisite for the reproducibility and repeatability of the sensor response.⁶ The thickness of Pt-DEB film can be estimated by Sauerbrey equation to be about 100 nm.

Organic vapor sensing performance

A typical real-time response of Pt-DEB coated QCM device to CHCl_3 is shown in Figure 5. The first stage was to make the sensor obtain a baseline in ambient air atmosphere. Then, the sensor was exposed to the sealed vessel with a certain volume of CHCl_3 . The CHCl_3 was evaporated freely and absorbed on the Pt-DEB polymer film to make frequency decrease until a steady-state was reached; indicating that maximum adsorption onto the QCM surface was obtained. After each concentration, the device was put out of the vessel. The CHCl_3 was finally flushed out of the sensor by ambient air atmosphere, and the frequency of QCM sensor returned to its baseline. Each absorption and desorption cycle took about 700 s. Fast response and recovery with good repeatability were observed at room temperature as shown in Figure 5. However, the baseline signal was not totally recovered to the initial level, which indicated that the analyte was not completely flushed out of the sensor when using ambient air to recover the sensor signal. Reproducibility was observed when a second drop of 6.7 ppm of CHCl_3 was introduced into the sensor chamber. It was found that the Pt-DEB-based sensor produce response of the same magnitude.

Using the same method, the responses of Pt-DEB-based QCM sensor to tetrahydrofuran, acetone, isopropyl alcohol, ethanol, and methanol were studied. Real-time responses for isopropyl alcohol, ethanol,

methanol, and tetrahydrofuran are shown in Figure 6. As can be seen, Pt-DEB presents sensitivity to all of the analytes, but shows low selectivity to different vapors. Previous investigations^{13,14} on the sensing properties of organometallic polymers compared with homologous organic ones, have shown the role of the transition metal in enhancing the sensitivity of the polymeric membrane toward chemicals in the vapor phase.

The real-time response curves to all of the analytes are similar. In general, it is considered that gas permeation occurs by three "solution-diffusion" steps, i.e., absorption, diffusion, and desorption process.¹⁵ The frequency decreases sharply with time initially when Pt-DEB film contacts with vapors, which results from surface adsorption effect. Then, the frequency increases slowly, mainly resulting from bulk diffusion effect. The interaction process between sensitive film and the adsorbed vapors is a dynamical process. When the sensor is exposed to vapors, both adsorption and desorption processes occur simultaneously. After reaching dynamic equilibrium, the number of adsorbed vapor molecules will be equal to the number of desorbed vapor molecules. Then, the frequency attains a stable value. The recovery also shows a slow decrease followed by a rapid increase of frequency when the vapors are desorbed, which is also due to surface effect and bulk effect.

To compare the sensitivity, frequency shifts versus corresponding concentrations of the organic vapors are plotted in Figure 7. It is obvious that the frequency shifts increase almost linearly with the increase of organic analyte concentrations.

It is apparent that the sensitivity of Pt-DEB (dissolved in CHCl_3), for CHCl_3 is much higher than for other analytes in Figure 7. We postulate that the highest sensitivity to CHCl_3 of Pt-DEB film could be attributed to the presence of chemisorbed molecular tunnels or holes on the polymer surface. They were formed during spin coating process used CHCl_3 as solvent for Pt-DEB bulky material. As it is well known that organic molecules can form a shell covering the polymer by exerting the strongest interaction with vapor molecules of the same type, and solvent-functionalization effect is responsible for this phenomenon.¹⁶

As shown in Figure 7, the frequency shifts of the Pt-DEB-coated QCM sensor for the alcoholic organics are, apparently, in the following order: isopropyl alcohol > ethanol > methanol. This result indicates that a larger molecular weight of alcohol has a higher sensitivity, which is in good agreement with the previous findings in Ref. ¹⁷. It is reasonable to assume that if the number of adsorbed molecules on an adsorbent is limited and identical for various adsorbates, a greater molar mass of adsorbate would certainly lead to a larger frequency shift.

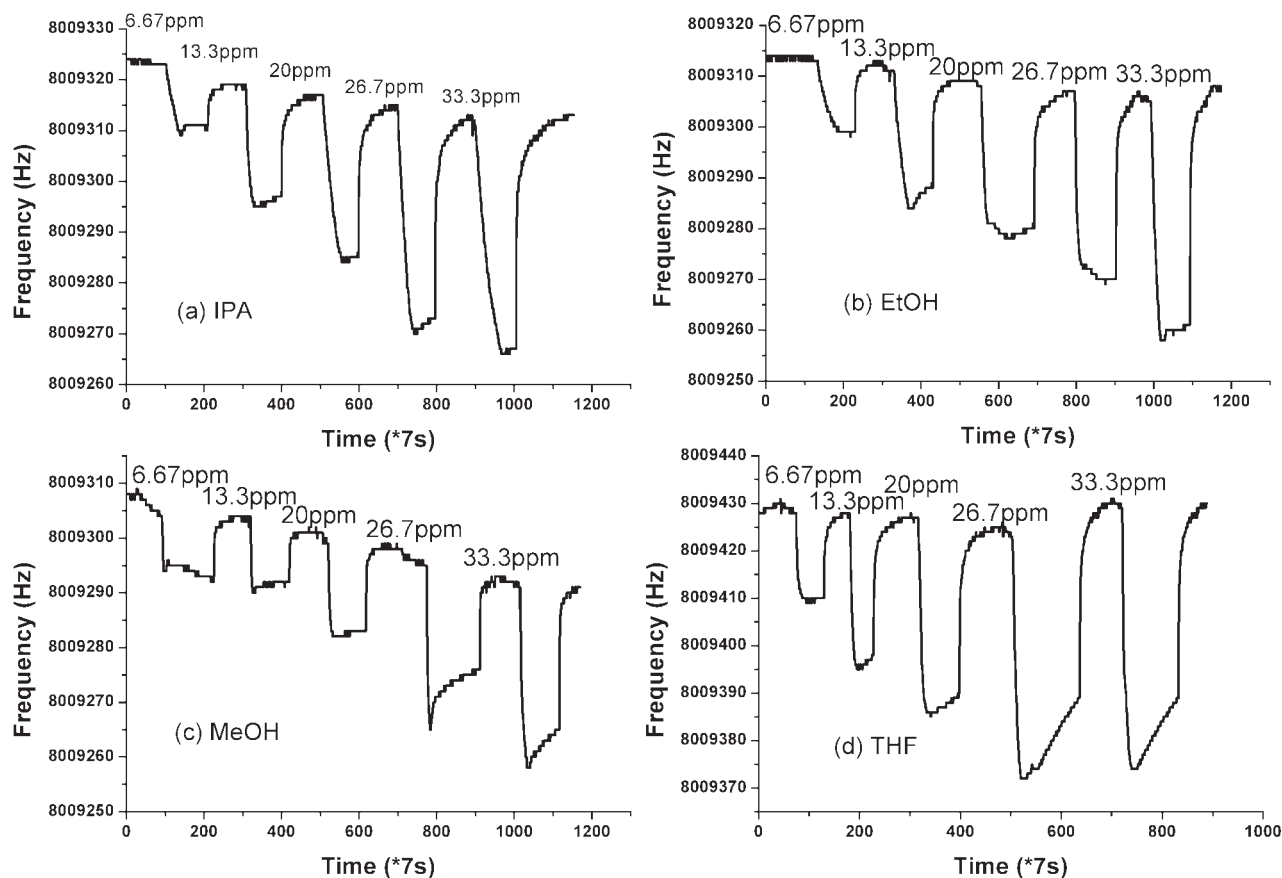


Figure 6 Real-time response of the Pt-DEB-based QCM sensor to: (a) isopropyl alcohol (IPA), (b) ethanol (EtOH), (c) methanol (MeOH), and (d) tetrahydrofuran (THF).

For a comparison, two various polar-organic molecules containing the propyl group, e.g., isopropyl alcohol and acetone, are selected in Figure 7. The frequency response of the sensor for these organic vapors is in the following order as isopropyl > acetone. This may be result from the formation of

strong hydrogen bonds as isopropyl molecules interact with Pt-DEB molecules due to the presence of $-\text{OH}$ group; however, there is no hydrogen bond formation between acetone and Pt-DEB.¹⁸

Detection limit of the Pt-DEB-based sensor for organic vapors

The detection limits of Pt-DEB-based QCM sensor for various organic vapors were also studied. To estimate the limit of detection (LOD was defined by a ration of $3\sigma/(\text{sensitivity})$),¹⁹ we measured the noise σ by linear regression of baseline frequency

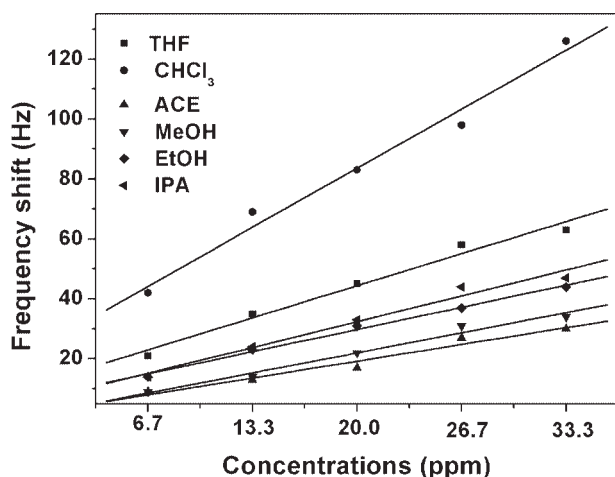


Figure 7 Frequency shifts versus concentrations of organic vapors.

TABLE I
Detection Limits of Various Organic Vapors with the Pt-DEB-Based QCM Sensor at Room Temperature

Organic vapors	Sensitivity (Hz/ppm)	Detection limit (ppm)
Tetrahydrofuran	1.61	1.87
Trichloromethane	2.96	1.00
Acetone	0.84	3.56
Methanol	1.00	3.00
Ethanol	1.11	2.70
Isopropyl alcohol	1.29	2.33

data over a period of ~ 5 min. The measured frequency noise was 1 Hz. Sensitivity can be estimated from the slope of working curve as shown in Figure 7. For instance, the detection limit for CHCl_3 can be estimated to be ~ 1.00 ppm from an analytical sensitivity of 2.96 Hz/ppm. The detection limits of Pt-DEB-based QCM sensor for various organic vapors are summarized in Table I. It can be seen that the Pt-DEB-based QCM sensor obviously exhibited a good sensitivity with the detection limits of ~ 1.0 – 3.56 ppm for various organic vapors at room temperature. The LOD of Pt-DEB-based QCM gas sensor is clearly lower than the carbon nanotubes based surface acoustic wave (SAW) gas sensor reported in the literature.¹⁶

Stability of Pt-DEB-based sensor during 30 days

To investigate the life-time of the polymer used for gas sensing, we detected the stability of Pt-DEB-based sensor during 30 days. The sensor was exposed to 6.7 and 33.3 ppm CHCl_3 , respectively, every 3 days. The experimental results demonstrate that the response of the Pt-DEB-based sensor to the same concentration CHCl_3 remained almost constant. The Pt-DEB-based sensor for CHCl_3 detection has good stability.

CONCLUSIONS

Poly-(bistriethylphosphine)-platinum-diethynylbenzene (Pt-DEB) was synthesized based on dehydrohalogenation reaction and deposited on QCM to study its gas sensitivities to different organic vapors at room temperature. Pt-DEB shows good reversibility, reproducibility, and linearly sensitivity but low selectivity to several organic vapors. The sensitivity of Pt-DEB (dissolved in CHCl_3) for CHCl_3 is clearly higher than that for foreign analytes and a larger molecular weight of alcohol has a higher sensitivity response. The detection limits of

Pt-DEB-based QCM sensor for various organic vapors range from 1.0 to 3.56 ppm at room temperature. Therefore, gas sensors based on Pt-DEB polymer are very promising for environmental and industrial applications. In further work, we will use N_2 as balance gas and study the influence of other gas in the ambient air.

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