

Multichannel Monolithic Quartz Crystal Microbalance Gas Sensor Array

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Multichannel Monolithic Quartz Crystal Microbalance (MQCM), in which an array of electrodes is fabricated on a monolithic quartz wafer, is a very attractive approach for miniaturization using Micro-Electro-Mechanical Systems (MEMS) technology for high throughput chemical or biological sensor systems. In this paper, we demonstrate and validate a monolithic QCM sensor array for gas detections. The monolithic QCM sensor array chip was fabricated using a simple, straightforward method. Four pairs QCM electrodes on a single AT-cut 10 MHz quartz plate were fabricated in both symmetric and asymmetric designs. Their resonance and sensing properties were thoroughly characterized and compared with a single regular QCM under the same conditions by using parallel multichannel QCM instruments. It is confirmed that each QCM in the MQCM behaves like an independent oscillator that responds to mass and/or viscosity change. Various factors that may affect the MQCM performance, such as the fabrication design, the numbers of oscillated electrodes in one MQCM, and the concentration of target analytes, were studied. Finally, the MQCM electrodes were selectively coated with an assortment of sensing films (ionic liquids (BMICS, BMIBF₄) and conductive polymer poly(vinyl ferrocene) (PVF)). Their applications capabilities for classification and detection of Volatile Organic Compounds (VOCs, i.e., ethanol, CH₂Cl₂, hexane) and water were studied. Our results show that the single-chip, multichannel QCM is a feasible and promising technology for a miniaturized, highly sensitive multianalysis system that can lead to substantial reductions in cost, analysis time, and sample volume.

The history of Quartz Crystal Microbalance (QCM) began in 1880 when Pierre and Jacques Curie discovered the piezoelectric or “pressure/electric” effect, where pressure exerted on a small piece of quartz causes an electrical potential difference between the deformed surfaces. The essence of QCM as an analytical tool lies in its ability to detect mass deposited on crystal surface and act as a sensor. Interfacial mass changes can be related to changes in the QCM oscillation frequency by applying Sauerbrey’s equation

(eq 1),¹ where n is the overtone number, μ_q is the shear modulus of the quartz ($2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$), and ρ_q is the density of the quartz (2.648 g cm^{-3}). It is assumed that the foreign mass is strongly coupled to the resonator.

$$\Delta f = \frac{-2\Delta m n f_0^2}{A(\mu_q \rho_q)^{1/2}} \quad (1)$$

Because of their small size, high sensitivity and stability, low weight, low cost, and low power requirements, piezoelectric crystals have been used as microbalances for the determination of thin-layer thickness and in general gas-adsorption studies.^{2,3} The incorporation of various chemically sensitive layers has resulted in the explosive growth of piezoelectric sensors.⁴ Also, EQCM, or the combination of QCM with electrochemical methods, has become a powerful tool for studying metal-electrode interfacial phenomena. In the past decade, QCM has been widely explored as transducers for monitoring a plethora of biospecific interactions, including enzymatic reactions, DNA interactions, protein–ligand interactions. QCM based sensors were developed for the detection of biomarkers,^{5,6} drug targets, virus capsids, bacteria, and living cells. Despite the versatile utility of QCM, the application of QCM in high throughput multianalytes analysis has been delayed because of challenges in fabricating functional devices with multiple QCMs or QCM arrays that can easily be integrated into microfluidic systems.

The concept of a sensor array with several QCMs fabricated on a monolithic quartz crystal plate was first reported by Tatsuma and his co-workers in 1999.^{7,8} Monolithic QCM (MQCM) is very attractive for various chemical and biological sensor applications using a QCM approach. An MQCM device would permit integration with a microfluidic system, which can lead to substantial reductions in cost, diagnostic time, and sample volume. Furthermore, Sauerbrey’s equation shows that reducing the electrode size will result in increased sensitivity. Together, these factors encour-

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age the implementation of an array of miniaturized electrodes on a single quartz crystal device, greatly expanding functionality relative to common one-electrode QCM devices that are commercially available. However, there are few reports of MQCM devices or their applications in real chemical and biological sensor systems. This is partly due to concerns of frequency interference between adjacent electrodes on a MQCM device. Shen et al. have shown several methods in the design of the devices that could suppress the frequency interference.⁹ For example, the microbalance channel can be designed to have different electrode sizes or have larger interchannel separation to avoid strong interference. Tatsuma et al. made a MQCM with different quartz thicknesses by preparing etched and non-etched regions on a single QCM chip.⁷ Using deep Reactive Ion Etching (RIE), Takashi et al. were able to fabricate a multichannel QCM sensor that has different resonance frequencies on a single quartz plate.⁸ These studies show that adjacent electrodes on the same quartz crystal substrate produce negligible interference when appropriately positioned.^{10,11} Recently, an "electronic nose" based on a multichannel QCM using a multiplex oscillator was reported.¹² Although each of the above multichannel devices has more than two QCM electrodes fabricated on one quartz plate, no more than two QCM electrode channels have been monitored simultaneously. In this report, we present a multichannel MQCM array that can be easily fabricated and can simultaneously record responses from all channels without interference from each other. Four QCM electrodes on a single AT-cut 10 MHz plate were fabricated in both symmetric and asymmetric geometrical designs. Their resonance and sensing properties were thoroughly characterized by simultaneously monitoring each of the MQCM electrodes and then comparing with results obtained using a single QCM monitored at the same time under the same conditions using parallel multichannel RQCM instruments. It has been confirmed that each QCM in the MQCM behaves like an independent oscillator that responds to mass and/or circumstance's viscosity change. Various factors that may affect the MQCM performance such as the fabrication design, the numbers of oscillated electrodes in one MQCM, and the concentration of target analytes were studied. Finally, the MQCM electrodes were coated with an assortment of selective coatings (ionic liquids (BMICS, BMIBF₄) and conductive polymer poly(vinyl ferrocene) (PVF)), and their application in classification and detection of VOCs (ethanol, CH₂Cl₂, or hexane) and water was studied. Our results show that a single-chip, multichannel QCM is a feasible and promising technology for highly sensitive multianalysis systems.

MATERIALS AND METHODS

Chemicals and Materials. All organic compounds (dichloromethane, ethanol, and hexane) were analytical reagents, purchased from Sigma-Aldrich Inc. and used as received. Ionic liquid butylmethylimidazolium camphorsulfonate (BMICS) was provided by Dr. Rex Ren at IL-TECH Inc. (Middletown, CT) with over 98% purity. Ionic liquid butylmethylimidazolium tetrafluoroborate

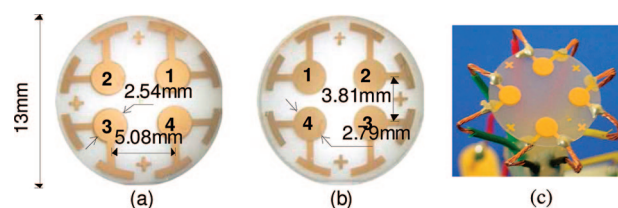


Figure 1. Photos of the fabricated asymmetric MQCM array, front side (a), backside (b), and a photo of the symmetric MQCM sensor array (c).

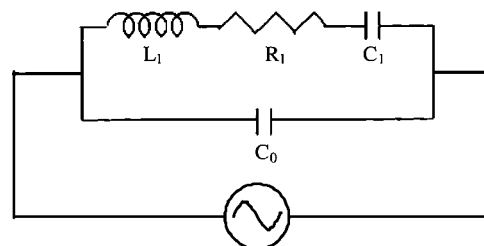


Figure 2. BVD equivalent circuit of a QCM. C_0 and C_1 are capacitances; L_1 is an inductance; and R_1 is a resistance.

(BMIBF₄) was purchased from Sigma-Aldrich Inc. with purity over 97%. Poly (vinylferrocene) (PVF) was purchased from Polysciences Inc. Eighteen M Ω Millipore purified water was used for all the aqueous solutions.

Fabrication of Monolithic QCM Array. Two different 2×2 arrays of small electrodes were designed and fabricated on 13 mm-diameter 166 μ m-thick 10 MHz AT-cut quartz plates (International Instruments Inc., OK). Both arrays were populated by four pairs of electrodes on both sides of a quartz plate, one with symmetrical electrode placement, the other with asymmetry in one dimension. On both devices, the front-side electrodes were 2.54 mm in diameter, and the backside electrodes were 2.79 mm to provide alignment tolerance during fabrication. For the symmetrical device, the center-to-center spacing between all adjacent electrodes was set to 5.08 mm. As shown in Figure 1, for the asymmetrical device, the electrode spacing was reduced to 3.81 mm in one dimension, while the other was kept to be 5.08 mm. Contact leads to all electrodes were routed to the edge of the quartz plate. To avoid undesired electric fields across the quartz plate because of contact traces, the front-side electrodes were routed to the top and bottom and the backside electrodes to the left and right. This orientation is shown in Figure 1.

The quartz was cleaned with Aqua regia, acetone, isopropanol, and deionized water. The arrays were fabricated using thin film deposition and photolithography. Two optical masks (produced by Infinity Graphics, Okemos, MI) were designed for each device, one for the top pattern and one for the bottom. The electrodes were deposited and patterned on each side of the quartz plate using the lift off technique: first photoresist was spun on each side and patterned using photolithography. Then, 5nm Ti/ 100nm Au thin film was deposited on each side using thermal evaporator. Finally, the photoresist was removed to lift off the undesired metal and produce the electrode pattern. Each pair of gold electrodes was connected to sockets by copper wires and conductive epoxy glue (Chemtronics). A picture of the final soldered four-channel QCM sensor array is shown in Figure 1c.

Modification of Each QCM. To test the behaviors of each QCM, BMICS, BMIBF₄, and PVF thin films were cast on three

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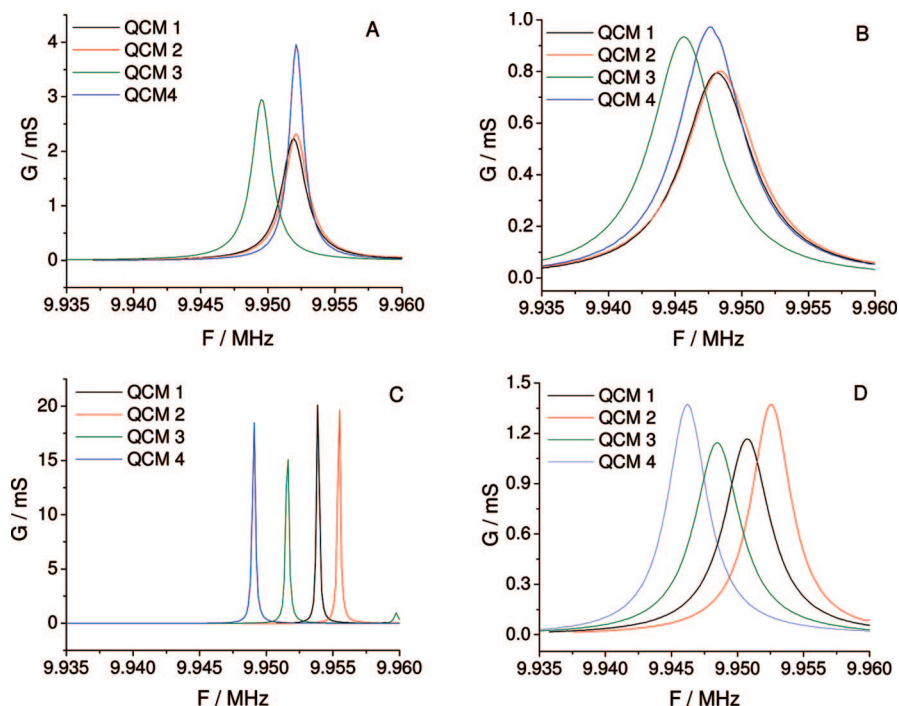


Figure 3. Conductance spectra of each QCM. (A) Symmetric MQCM in air, (B) symmetric MQCM in water, (C) asymmetric MQCM in air, and (D) asymmetric MQCM in water.

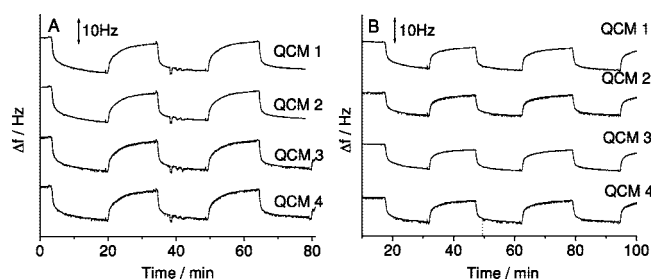


Figure 4. Time course response curves obtained from each QCM of the symmetric (A) and asymmetric (B) MQCMs when exposed to 10% ethanol vapor.

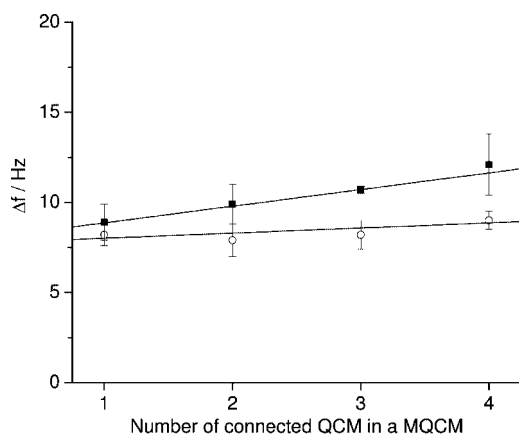


Figure 5. Representative frequency changes of QCM 4 in the symmetric (■) and asymmetric (○) MQCMs tested with 10% ethanol when there were one, two, three, and four of these four QCMs connected.

of the four QCMs from their solutions in ethanol and dichloromethane, respectively, on only one side. Extreme care was taken to keep the cast thin films within each electrode.

Therefore, there was no mutual contamination between neighbor electrodes. After the casting, the solvents were dried in air before the gas sensing experiment. The resonance frequencies of each QCM before and after the coating, along with the total amount of the coating, are shown in Table 1.

Gas Flow and Measuring Systems of the Monolithic QCM Sensor Array. The MQCM gas sensor array setup was similar to that described in our previous publication.¹³ Briefly, the flow rates of the N_2 carrier gas were controlled by two digital mass-flow controllers (MKS Instruments Inc.). A total gas flow rate of 100 mL/min was used. The first N_2 flow bubbled through a reservoir of samples and was saturated by the sample's vapors, then it was diluted by a second N_2 flow, and the final concentration was calculated based on the ideal gas laws. The percentage within the results is the percent of saturated vapor pressure. The diluted sample gas flowed through a tubing about 1 m in length, then into the sensor chamber. The gas sensing chamber has a tubular structure. The MQCM sensor array chip was placed horizontally at about the halfway between the gas inlet and outlet in the chamber facing directly to the gas inlet at the bottom of the chamber. The gas outlet is located on the top of the chamber. In the experiments in which a coating was applied to each of the MQCM array electrodes, we only coated the gold surface facing the gas inlet. Therefore, the distances of four MQCMs to the gas entry are almost identical. This experimental consideration will allow the gas sample to reach the four QCMs almost simultaneously. We used a slow gas flow rate in our experiment so that all QCMs could reach equilibrium in each detection cycle. The glass tubing and the sensor chamber were located in a GC oven, where the temperature was precisely controlled. Mextec RQCM instru-

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Table 1. Resonance Frequency of Each QCM before and after the Coating and the Total Amount of the Coating

	electrode coating	QCM1 bare gold	QCM2 BMICS	QCM3 BMIBF ₄	QCM4 PVF
Symmetric MQCM	f_0 before coating (MHz)	9.951800	9.952100	9.951850	9.947750
	f_0 after coating (MHz)		9.943750	9.945050	9.932150
	Amount of coating (nmol)		22.6	30.0	73.6
Asymmetric MQCM	f_0 before coating (MHz)	9.952300	9.952600	9.957500	9.946200
	f_0 after coating (MHz)		9.945000	9.948950	9.938450
	Amount of Coating (nmol)		20.5	7.9	36.6

Table 2. Value of Each Element in BVD Circuit Measured in Air and in Water

	symmetric MQCM in air					asymmetric MQCM in air				
	1	2	3	4	average	1	2	3	4	average
R_1 (Ω)	448	338	433	254	368 ± 90	52	45	42	50	47 ± 5
L_1 (mH)	33	30	33	33	32 ± 2	35	32	33	32	33 ± 1
C_1 (fF)	7.8	8.5	7.9	8.1	8.1 ± 0.3	7.3	8.0	7.9	8.1	7.8 ± 0.4
C_0 (pF)	5.9	6.0	6.2	6.1	6.1 ± 0.1	7.2	6.3	6.1	6.2	6.5 ± 0.5

	symmetric MQCM in water					asymmetric MQCM in water				
	1	2	3	4	average	1	2	3	4	average
R_1 (Ω)	1262	1089	1258	1158	1192 ± 84	862	728	888	700	795 ± 94
L_1 (mH)	32	28	31	27	30 ± 2	33	32	33	32	33 ± 0.6
C_1 (fF)	7.9	9.0	8.3	9.5	8.7 ± 0.7	7.7	8.1	7.8	8.0	7.9 ± 0.2
C_0 (pF)	5.9	6.1	6.2	6.6	6.2 ± 0.3	6.3	6.3	6.1	6.1	6.2 ± 0.1

Table 3. Frequency Change of Each QCM When Exposed to 10% Ethanol Vapor

	QCM 1	QCM 2	QCM 3	QCM 4
Symmetric MQCM				
average frequency change/Hz ($n = 3$)	12.5 ± 1.9	12.3 ± 2.0	12.3 ± 1.5	12.1 ± 1.7
Asymmetric MQCM				
average frequency change/Hz ($n = 3$)	9.2 ± 1.0	8.6 ± 0.8	8.3 ± 10.7	9.0 ± 0.5

ments were used to measure the resonant frequency and the damping resistance for all experiments.

RESULTS AND DISCUSSION

Test MQCM by Network Impedance Analyzer. We have studied the electrical characteristics of the fabricated MQCM quartz electrodes and compared them with a single QCM electrode by Network Impedance Analyzer (NIA). The diameter of the single gold QCM electrode is 5.10 mm with 1000 Å Au coated directly on both sides of the non polished quartz plate. Even though the single gold QCM electrode is bigger in diameter than each of the MQCM gold quartz electrodes, the quartz plate has identical size and properties (AT cut, etched with diameter of 13.67 mm). Each electrode pair of either the fabricated MQCM electrodes or single QCM electrode was connected to the driving circuit of a NIA (Agilent 4395A). The MQCM electrodes showed a resonance frequency of around 10 MHz, as expected. Spurious modes at around the 30 MHz and 50 MHz band can be observed along with the fundamental mode at around 10 MHz. The single QCM electrode shows the similar conductance versus frequency spectra. The difference is that the conductance intensity is higher for a single QCM electrode than for any of the MQCM electrodes.

The observed signal quality was sufficient to demonstrate the feasibility of the current MQCM array design. Further optimization of MQCM electrode designs may be possible by adjusting electrode positions and using finite element analysis on the electrode system.

The piezoelectric characteristics of a QCM could be represented by the Butterworth-van-Dyke (BVD) equivalent circuit,^{4,14} as shown in Figure 2. A NIA was used to measure the value of the four elements, R_1 , L_1 , C_1 , and C_0 , in the BVD circuit of each MQCM electrode. The NIA applies alternative electric power in a frequency (F) range on the QCM, and measures the admittance (Y) (that is, the inverse of the impedance (Z)), and the real part (conductance, G) and imaginary part (susceptance, B) of the admittance.¹⁵ Values of four elements in the BVD circuit were obtained by fitting the conductance spectra (G vs F) to the BVD equivalent circuit. Typical conductance spectra and results of the parameters of each QCM in air and in water are summarized in Figure 3 and Table 2.

As shown in Figure 3, for both symmetric and asymmetric MQCMs, all the conductance versus frequency spectra have a Gaussian shape with the fundamental resonance frequency close to 10 MHz. These results are similar to a typical single QCM electrode. In the asymmetric design, each of the QCM electrodes has different resonance frequencies. In the symmetric design, there are three electrodes that have similar resonance frequencies. Previous MQCM studies often attempted to create gold electrodes with different thicknesses so that they will have different resonance frequencies. It was viewed that MQCMs with the same frequencies were likely to interfere with each other. We intended to further understand and compare the characteristics of the

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Table 4. Average Frequency Change upon Exposure to 10% Ethanol When Different Numbers of QCMs in a MQCM Were Connected

	single QCM	MQCM array			
		QCM 1	QCM 2	QCM 3	QCM 4
symmetric MQCM		12.5 ± 1.9	12.3 ± 2.0	12.3 ± 1.5	12.1 ± 1.7
	5.4 ± 1.4		10.3 ± 0.4		10.7 ± 0.2
	5.1 ± 0.9			10.9 ± 1.0	9.9 ± 1.1
asymmetric MQCM	5.6 ± 0.2				8.9 ± 1.0
		9.2 ± 1.0	8.6 ± 0.8	8.3 ± 10.7	9.0 ± 0.5
	5.7 ± 1.3		8.9 ± 0.8	8.7 ± 0.7	8.2 ± 0.8
	6.3 ± 2.5			8.2 ± 0.8	7.9 ± 0.9
	4.7 ± 0.7				8.2 ± 0.6

MQCM performance. We used parallel QCM oscillators to measure simultaneously each of the four MQCM electrode oscillations, to determine whether there was interference between each of the MQCM electrode while they oscillated at the same time. Figure 3 also shows that, at the resonance frequency, the conductance value and the peak width at half-height decreased significantly when one side of the MQCM electrodes was in water. This was due to the significant increase of the damping resistance R_1 when water was added (see Table 2). As expected, the absolute resonance frequency of all electrodes decreased after water was introduced to their surfaces. Inductance and capacitances did not change significantly, and the order of the peaks did not change either. These characteristics in both air and water resembled those features of a single QCM. Therefore, each QCM in the MQCM can be considered as an independent QCM in a MQCM sensor array.

Simultaneous Monitoring of 4-Channel MQCM of Both Symmetric and Asymmetric Designs. When each pair of the MQCM electrodes was connected to the multichannel Mextec RQCM instruments, each of the four QCMs showed stable oscillation simultaneously. Therefore, upon exposure to 10% ethanol vapor, four sensorgrams of a MQCM were obtained at the same time. Figure 4 shows a typical time course of the sensorgrams obtained from a symmetric MQCM and an asymmetric MQCM. It can be seen that sensorgrams from each QCM have a very stable baseline and a reproducible response to the same analyte. The frequency change of each QCM in one MQCM was very close (see Table 3). The average response to 10% ethanol was in the range of 12.1–12.5 Hz for the symmetric MQCM and 8.3–9.2 Hz for the asymmetric MQCM. This result may suggest that the four QCMs in each MQCM can give identical response to the same analyte. However, the responses from symmetric MQCM were larger than that of asymmetric MQCM. This may be due to a slightly difference in roughness of the gold electrode on the quartz surface, although each QCM in the MQCM has an identical geometric area in all cases.

Cross Interference between the Individual QCMs in One MQCM. To further test if the four QCMs in a MQCM worked independently upon exposure to the analyte when monitored simultaneously, frequency changes upon exposure to 10% ethanol vapor at the following conditions were studied and compared. First, QCM1 in the MQCM was disconnected and replaced with a regular single 10 MHz QCM. Sensorgrams of the single QCM and the other three QCMs in the MQCM were recorded. Second, another of the original MQCMs was disconnected. Sensorgrams of the regular QCM and the other two QCMs in the MQCM were

recorded. Third, another QCM electrode in the MQCM was disconnected, to leave only one electrode out of four in the MQCM. The MQCM was connected to oscillation circuits, and sensorgrams of the regular single QCM and the remaining QCM in the MQCM were recorded. In all these experiments, the connected QCMs gave a stable baseline and a reproducible response to the same analyte. The values of the frequency changes are summarized in Table 4 and Figure 5.

In all the cases, the regular single 10 MHz QCM yielded the lowest response to the same analyte. As described by the Sauerbrey equation, the frequency change is proportional to the mass load on a unit geometric area. Thus, a smaller area could lead to a higher response. Another possible interpretation is that the MQCM may have had more electrode roughness compared to the single QCM electrode. The gold deposition conditions for MQCM fabrication in our laboratory are different from those used for the manufacturing of a regular single QCM (International Instruments Inc., OK). Therefore, within each unit surface area, more analyte molecules could have been absorbed in the MQCM electrodes and thus produced a bigger response. In addition, in all the MQCMs, electrodes on one side are slightly larger than their counterparts on the other side for the sake of better alignment during deposition. This difference may also contribute to the larger response from the MQCM, compared with the single regular QCM. As shown in Table 4 and Figure 5, there are few differences in response when one or more of the MQCM electrodes were connected to the oscillation circuits in the asymmetric design. The differences were slightly larger in the symmetric design. Our study shown in Figure 7A,B below suggests that this slight mean value change of the frequency in the symmetric MQCM array has little effect for the MQCM gas sensor array performance.

MQCM Responses versus Vapor Concentration. Figure 6a and Figure 6b show results from a symmetric MQCM array and an asymmetric MQCM array exposed to ethanol vapor in concentration of 10%, respectively. Again, each QCM in the MQCM array produced a stable baseline and reversible and reproducible responses. Figure 6c presents frequency changes from the symmetric MQCM array (A) and the asymmetric array (B) exposed to ethanol vapor in different concentrations. The frequency changes yielded a strong linear relationship to the ethanol concentration (Figure 6c): the coefficients of linearity by least-squares fit of the line were all greater than 0.945.

An interesting observation from Figure 6 is that the responses of the symmetric array are independent whereas the responses of the asymmetric array appear to be correlated to their relative

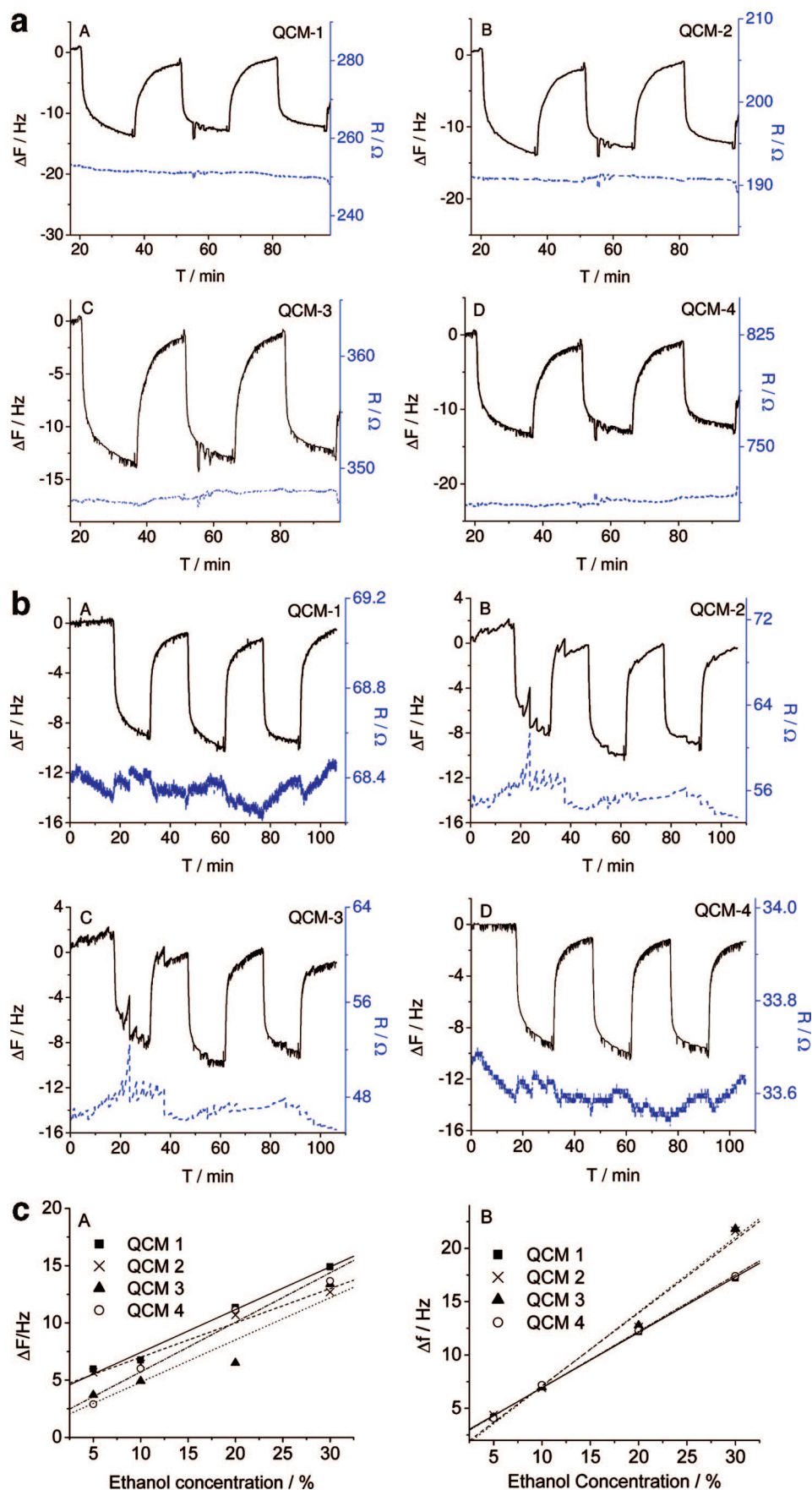


Figure 6. (a) Sensorgrams of four QCMs in symmetric MQCM array, 10% ethanol. (b) Sensorgrams of four QCMs in asymmetric MQCM array, 10% ethanol. (c) Frequency change versus ethanol concentration of each QCM in the symmetric MQCM array (A) and asymmetric MQCM array (B).

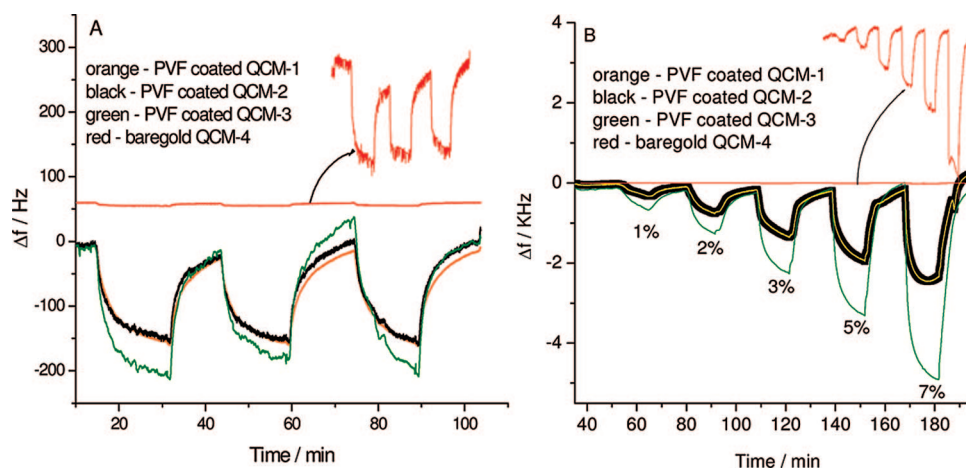


Figure 7. Sensorgrams of symmetric MQCM. QCM 1 is bare gold, QCM 2 and 3 are coated with 216 and 217 nm PVF, respectively, and QCM 4 is coated with 311 nM PVF. (A) response to 10% ethanol, and (B) response to 1%, 2%, 3%, 5%, 7%, and 10% CH_2Cl_2 .

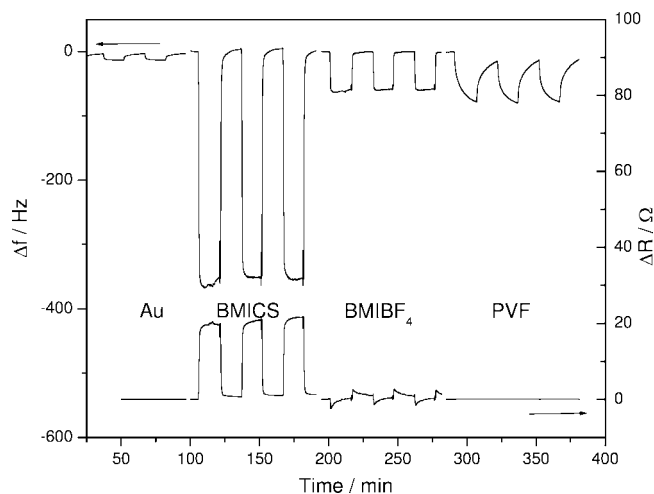


Figure 8. Sensorgrams to 10% ethanol obtained with an asymmetric MQCM. The four QCMs were either bare gold or coated with BMICS, BMIBF₄, and PVF, respectively.

geometry. In the asymmetric array, the responses of QCM 1 and QCM 4 are almost identical; likewise, the responses of QCM 2 and QCM 3 are almost identical. Note that the asymmetrical electrode layout places QCM 1 and QCM 4 closer to each other than to the other electrodes. Similarly, QCM 2 and QCM 3 are closer to each other. Thus, these results may indicate some cross-coupling between the closely placed electrode pairs, (QCM 1, QCM 4) and (QCM 2, QCM 3). However, no cross-coupling is observed between adjacent electrode pairs with greater spacing, (QCM 1, QCM 2) and (QCM 3, QCM 4).

MQCM Sensor Array for Classification and Quantification of Gases Using Selective Coatings. *Different Amounts of Polyvinylferrocene (PVF) Modified MQCM.* Using a symmetric MQCM, three of the four QCMs were coated with PVF. Two of them had the same amount of PVF, while the third had a larger PVF amount. The fourth was a bare, gold electrode (used as a control). The sensorgrams of this MQCM's response to 10% ethanol or to different concentrations of CH_2Cl_2 are shown in Figure 7A and B. It is obvious that the bare gold electrode showed the smallest response to the two analytes. The two electrodes that were coated with same amount of PVF showed almost the same response to

10% ethanol (Figure 7A), as well as the same response when they were exposed to the different concentrations of CH_2Cl_2 . As expected, the electrode with the larger amount of PVF showed the strongest responses to both 10% ethanol and CH_2Cl_2 at varying concentrations. These results show that the PVF modified QCMs have a much stronger response than unmodified QCM (bare gold), and that the enhancement of sensitivity depends on how much PVF was coated on the QCM. The more PVF that was coated on the QCM, the stronger the response to the analytes. This is because, as a polymer, PVF has high surface area and also can swell in response to ethanol and CH_2Cl_2 analytes, but ethanol and CH_2Cl_2 molecules only physically absorb on the gold surface.

MQCM Electrodes Selectively Coated with an Assortment of Sensing Films. When the surfaces of the QCMs were modified by different chemical coating, the four QCMs were no longer identical. Their responses to the same analyte will be different. Figure 8 shows typical asymmetric MQCM sensorgrams to 10% ethanol when the four QCMs were coated with ionic liquids BMICS, BMIBF₄, and PVF, respectively, or without coating (i.e., the bare gold electrode). Again, stable baselines and reproducible responses were observed on all four QCMs. Each time the ethanol vapor was switched on and off, it reached the equilibrium quickly.

The strength of the signals was different because the ethanol absorption and partition in the different surfaces varied. BMICS and BMIBF₄ are liquids and miscible with ethanol. Therefore, stronger signals were obtained using QCMs coated with these two ionic liquids than those with only bare gold electrode. PVF thin film has larger surface area compared with bare gold. PVF, as a polymer, can also be swollen by ethanol. Therefore, the frequency change from PVF coated QCM was larger than that from bare gold, since PVF is a solid polymer and the diffusion of ethanol molecules in a PVF film is relatively slow. Therefore, it takes longer time to reach equilibrium. As shown in Figure 8, there are little damping resistance changes upon exposure to an ethanol analyte for the bare gold and PVF coated MQCM electrodes, indicating the PVF films are rigid. As expected, the damping resistance changes upon exposure to ethanol analyte for BMICS and BMIBF₄ coated MQCM are bigger since adsorption

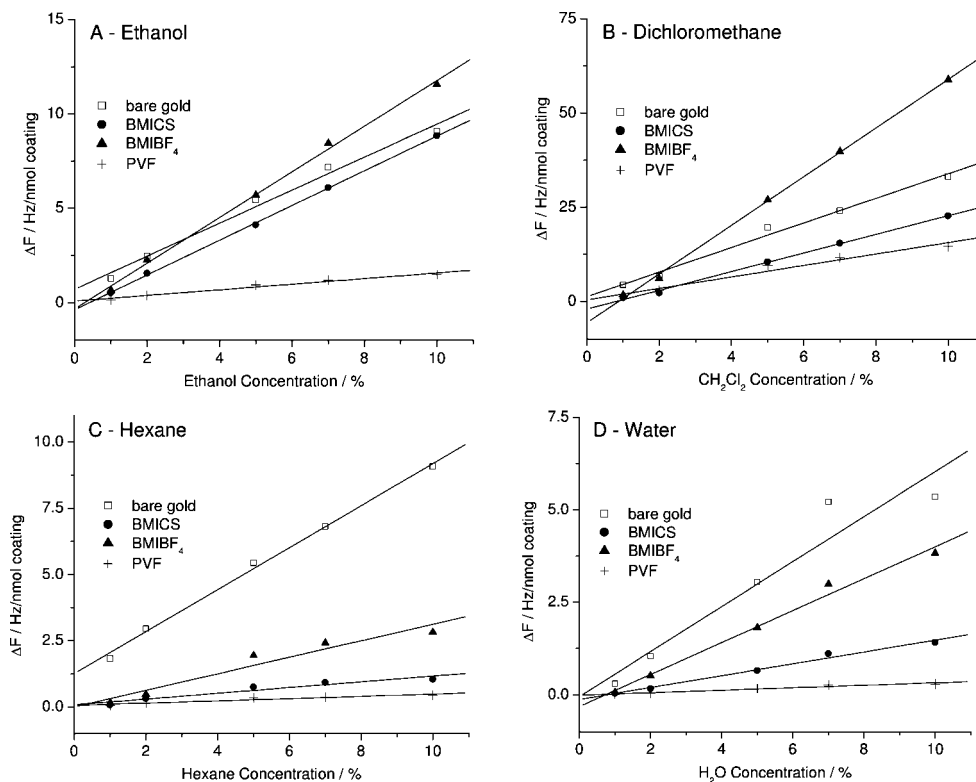


Figure 9. Calibration curves of ethanol (A), dichloromethane (B), hexane (C), and water (D) measured by MQCM arrays (bare gold and QCMs coated with BMICS, BMIBF₄, and PVF).

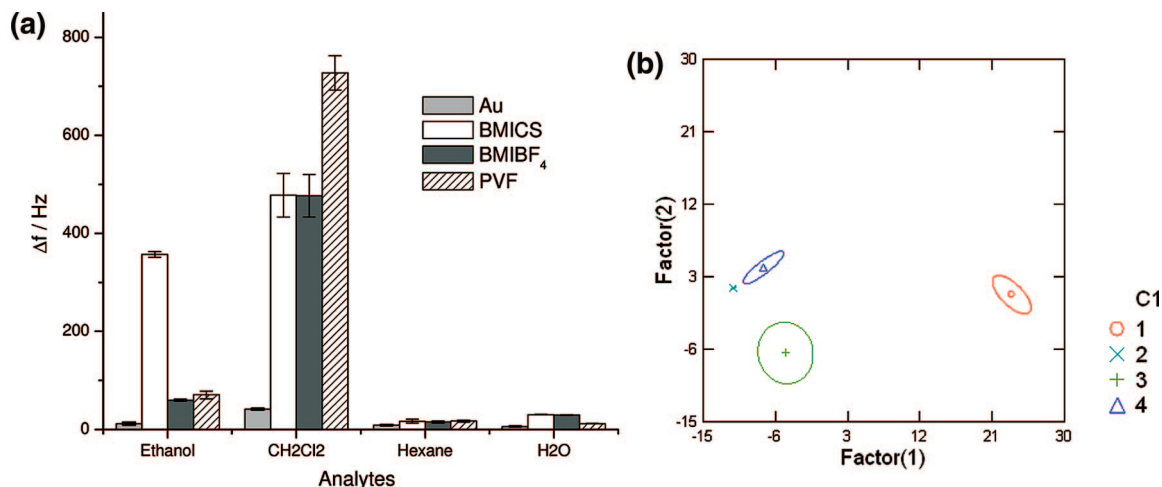


Figure 10. (a) MQCM response patterns of 10% ethanol, dichloromethane, hexane, and water. The three QCMs in the asymmetric MQCM were coated with BMICS, BMIBF₄ and PVF, respectively, and one was a bare gold electrode without any coatings. (b) LDA analysis of the pattern in (a) 1 - ethanol; 2 - hexane; 3 - dichloromethane; 4 - water.

of ethanol could also result in viscosity changes of the BMICS and BMIBF₄ coatings.

The MQCM electrode array with the various coatings described above were used to measure other organic vapors (dichloromethane and hexane) and water besides ethanol at various concentrations. The frequency changes were proportional to the concentration of the vapors in all cases. However, the slopes of the straight lines were different, indicating a different sensitivity of gas partition in the four modified MQCM surfaces. As shown in Figure 8, a bare gold electrode gave the smallest absolute frequency change. Figure 9 summarizes the results obtained from an asymmetric MQCM, in which the four MQCMs were bare gold

or modified with BMICS, BMIBF₄, and PVF coatings, respectively, upon exposures to the ethanol, dichloromethane, hexane, and water vapors. The frequency changes of the three QCMs that are modified by ionic liquids or PVFs are normalized by the amount of coating on each QCM. Therefore, the unit is Hz/nmol of coating. It can be seen that both ILs BMICS and BMIBF₄ coated QCMs showed stronger responses to all four vapors than the PVF coated QCM. The vapor molecules could be absorbed by the ILs as solutes since ILs are liquids. However, when PVF was used, the vapor molecules were adsorbed on the surface of the PVF film since PVF is more of a solid coating at room temperature. Bulk ILs, even thin films,

could absorb much more vapor molecules than Langmuir adsorption on a solid surface. This is also the reason why it takes a longer time for the PVF coated QCM to reach equilibrium. Comparing the two ILs, BMIBF₄ showed a stronger sensitivity to all four vapors, probably because of the lower viscosity of BMIBF₄ and relative higher solubility of the vapor analytes in BMIBF₄. The frequency change for a bare gold electrode can not be normalized since there is no coating on the bare gold. Therefore, comparing the frequency change on bare gold and normalized frequency changes on other coated QCMs is not meaningful. However, from Figure 7 and Figure 9, one can see that the response signals from bare gold were always weaker than those from other QCMs with coatings. This is also due to the very small amount of vapor molecules that were adsorbed on the gold surface by physical adsorption.

As our previous report¹⁶ details, BMICS has a camphorsulfonate anion, which contains a carbonyl group. The characteristic FT-IR peak of the carbonyl group is at 1741 cm⁻¹ for BMICS. After the adsorption of ethanol, the carbonyl peak blue-shifted to 1744 cm⁻¹. However, no peak shift of the carbonyl group vibration in either BMICS was observed upon adsorption of CH₂Cl₂, while it shifted to 1744 cm⁻¹ when ethanol was adsorbed. The carbonyl peak shifting was also not observed when heptane was adsorbed in BMICS. This result implies that a polar solvent interacts with the carbonyl of the camphorsulfonate anion. BMIBF₄ has the same cation as BMICS but a different anion BF₄⁻, which has symmetric structure and does not have the same strong interaction with ethanol compared to BMICS.

The above differences in sensitivity could also be represented by the response patterns of the MQCM to each vapor. Patterns of ethanol, dichloromethane, hexane, and water obtained at a 10% concentration with an asymmetric MQCM are shown in Figure 10. The patterns obtained with the same four QCMs are all different. These patterns are similar to that of when four single QCMs were used. The features of these patterns do not depend on the concentration of the vapors because of the excellent linearity of the calibration curves. On the other hand, the patterns do depend on the properties of the chemical coating used to modify the QCMs. These patterns are the "fingerprint" of the vapors. The canonical data clusters obtained with linear discriminant analysis (LDA), using SYSTAT 11 (SigmaPlot Inc.) are shown in Figure 10. Jackknifed Classification Matrix results show 100% accuracy for the classification of ethanol, hexane, and dichlo-

romethane, and 80% accuracy for the classification of water based on this MQCM array. Thus, with further coating optimization, classification or identification of unknown vapors could be achieved by pattern recognition using a simple MQCM array.

CONCLUSIONS

It has been demonstrated that the so-fabricated four-electrode MQCMs, with both a symmetric and an asymmetric design, showed promising characteristics as miniaturized multichannel QCM sensor arrays. Each QCM in the arrays could oscillate individually, responding as a gas sensor to VOCs reversibly and proportionally. Because the thickness shear wave decays exponentially beyond the electrodes, reducing the electrode area has little effect on the sensitivity of the QCM sensors. After being coated with either an ionic liquid or PVF, the responses of each QCM in the asymmetric MQCM were found to depend on the electrode geometry and the coating thickness. The analyte responses of individually coated QCMs in the MQCM arrays produce a response pattern that can be used to identify specific analytes. Similar results were obtained with a MQCM having a symmetric geometry. Therefore, both MQCM designs were found to be suitable for use as QCM sensor arrays. Our results indicate that MQCM sensor arrays show negligible cross-coupling, even in the symmetric design where several electrodes have similar oscillation frequency. This finding is highly significant because it contradicts the popular thought that each electrode of the MQCMs should be fabricated at varying thicknesses to reduce cross coupling. Our simple fabrication procedure provides an inexpensive and reproducible method to prepare miniaturized QCM sensor arrays. Future combination of MQCM arrays with microfluidics would provide an excellent opportunity to realize a chemical/biological sensor laboratory-on-chip.

ACKNOWLEDGMENT

This work is partially supported by the National Institute of Health Award R33EB000 672, Oakland University, JADI Inc., and the National Science Foundation under Award Number DBI-0649847. Xiaoxia Jin thanks the Provost Graduate Student Research Award of Oakland University. Ionic liquids used in this study are provided by Dr. Rex X. Ren at IL-Tech Inc., Middletown, CT. We thank Mr. Kuangyu Hou and Dr. Lei Yu for their help and contributions to this work.

Received for review September 4, 2008. Accepted November 11, 2008.

AC8018697

(16) Jin, X.; Yu, L.; Garcia, D.; Ren, R. X.; Zeng, X. *Anal. Chem.* **2006**, 78, 6980–6989.