

Chemical Sensor Based on Microfabricated Wristwatch Tuning Forks

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We report here a chemical sensor based on detecting the mechanical response of a thin ($\sim 10\text{-}\mu\text{m}$) polymer wire stretched across the two prongs of a wristwatch quartz tuning fork (QTF). When the fork is set to oscillate, the wire is stretched and compressed by the two prongs. The stretching/compression force changes upon adsorption of analyte molecules onto/into the polymer wire, which is detected by the QTF with pico-Newton force sensitivity. An array of such sensors with different polymer wires is used for simultaneous detection of several analytes and for improvement of pattern recognition. The low cost ($\sim 10\text{¢}$) of the QTF, together with that an array of QTFs can be driven to oscillate simultaneously and their resonance frequencies detected with the same circuit, promises a high performance, low cost, and portable sensor for detecting various chemical vapors. We demonstrate here detection of parts-per-billion-level water, ethylnitrobenzene, and ethanol vapors using the QTF arrays.

Recent advances in materials and devices have offered exciting new technologies for the detection of chemical vapors.¹ The use of modified metallic nanoparticles,² metallic and semiconducting nanowires,^{3–7} single-walled carbon nanotubes,^{8,9} polyaniline micro/nanostructures,^{10–12} and carbon–polymer composites^{13,14} has been reported. Discrimination of chemical vapors has been achieved

by using sensor arrays made of different conducting polymers or composites in combination with multivariate statistical techniques.^{15,16} These works are based on measuring the electrical properties of the sensing materials. Since most organic sensing materials are not conductive, measuring changes in their mechanical properties becomes an interesting choice. Well-established mechanical methods are surface acoustic wave (SAW), bulk acoustic wave (BAW), and quartz crystal microbalance (QCM), which detect mass/viscoelastic property changes due to specific and nonspecific adsorptions of chemicals.^{17–19} Another method uses microfabricated cantilevers by measuring either a bending or a shift in resonance frequency of the cantilever associated with the binding of analyte molecules on the cantilever.^{20,21}

We report here an alternative chemical sensor to measure mechanical properties of nonconductive polymer sensing materials using a microfabricated quartz tuning fork (QTF) array (Figure 1).²² We stretch a thin polymer wire (a few micrometers in diameter) across the two prongs of each QTF in the array (Scheme 1A). When the fork is set to oscillate, the wire is stretched and compressed by the two prongs. Upon adsorption or binding of the analyte molecules onto the polymer wire, a change in the mechanical force (stress) of the polymer wire occurs, which can be easily and sensitively detected as a change in the resonance frequency of the tuning fork (Scheme 1B).²² An array of such devices using different polymer wires can be used to simultaneously detect different analytes and to reduce false alarms.

Unlike the previously reported SAW, BAW, QCM, Fourier transform-QTF,²³ and microcantilever techniques that detect mass, viscoelastic properties, or surface stress changes, our sensor measures force changes in thin polymer wires. This approach is particularly suitable for detecting low molecular weight molecules because analyte binding anywhere along a wire can trigger a

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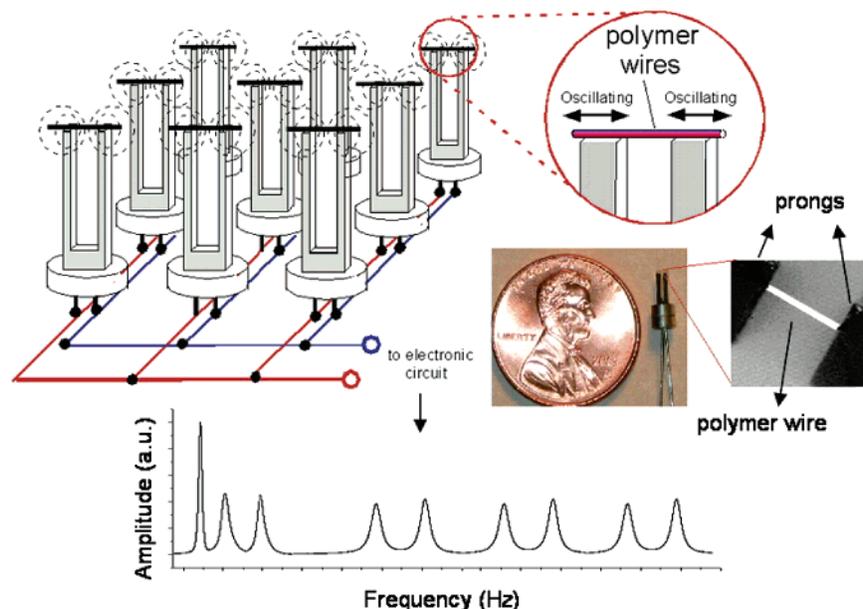
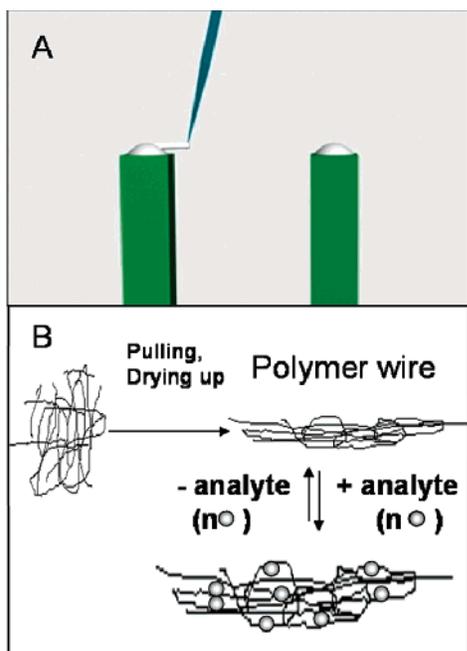


Figure 1. An array of microwire QTF sensors. Each wire is stretched across the two prongs of a quartz tuning fork. All the forks are connected to the same electronic circuit that can drive all the forks into resonance and detect the resonance frequencies at the same time. Lower right corner images show the scale of a typical quartz tuning fork and polymer wire.

Scheme 1. Schematic Representation of the TF Modification with Polymer Wire and of the Reversible Swelling of the Polymer Wire Structure in the Presence and the Absence of Analyte Molecules



(A) A polymer wire is bridged across the two prongs of a microfabricated tuning fork by pulling a polymer solution of appropriate viscosity. (B) The individual polymer chains in the wire are forced by capillary forces to align along the pulling direction during the drying step. The polymer wire tends to redissolve and relax to its original state in the presence of analyte molecules, which induces a stretching force in the wire.

change in the force of the entire wire. Commercial quartz tuning forks can achieve a force sensitivity of a few pico-Newtons (1 Hz bandwidth), much smaller than the force required to break

a single covalent bond. This extremely high force sensitivity is a reason that quartz tuning forks are preferred in noncontact atomic force microscopy to detect weak van der Waals forces.^{23,24} Since quartz is a piezoelectric material, one can simultaneously drive all the forks in the array to oscillate with a simple circuit, and the same circuit can simultaneously detect all the oscillations that are separated in frequency space in the fashion of an optical spectrum. This self-sensing capability does not require the external apparatus (e.g., optical or capacitive detections) used in microcantilever works,^{23,24} which simplifies the instrumentation and, more importantly, allows one to build a compact design of a QTF array for the device applications (Figure 1).

QTFs also have a number of other distinctive features. Their quality factor (Q) often exceeds 10 000 in air due to the superior properties of quartz crystals. This large quality factor, together with the noise cancellation mechanism of two identical prongs in the forks, results in an extremely high force sensitivity with minimal power dissipation. QTFs are also astonishingly stable over time and temperature,²⁴ which is the reason that the time deviation of even a cheap toy watch is no more than a few seconds a week. Billions of QTFs are manufactured annually for time-keeping devices at a cost of a few cents each. The commercial QTFs are well-packaged with convenient electrical wiring options, and the electronic circuits for driving and sensing the resonance have been optimized and miniaturized over years by the watch industry.

In the present work, we show that the above-mentioned properties of QTFs can be combined with polymeric wires to build a simple, reusable, and sensitive sensor for chemical vapor detection. We have used different polymer materials to sense different vapors. For example, polyvinylphosphonic acid is particularly good for monitoring relative humidity, while wax provides

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sensitive detection of nitrobenzene derivatives. The use of an array of different polymer wires provides additional pattern recognition.

MATERIALS AND METHODS

QTFs. QTFs with a resonance frequency of 32.768 kHz (dimension: $4 \times 0.25 \times 0.6$ mm³) were purchased from Newark Electronics. These QTFs have an effective spring constant of ~ 20 kN/m and a thermal noise as small as $\sim 4 \times 10^{-4}$ nm (rms oscillation amplitude of the prongs) at room temperature.²⁴ The Q is typically 8000 before polymer wire attachment. After stretching polymer wires across individual QTFs (Scheme 1A), their resonance frequencies increase to different values, and the Q s decrease to 10–40% with respect to the original value; however, Q values remain large enough to perform precise resonant frequency shift determinations.

Instrumentation. An AC modulation from a function generator (Stanford Research Systems, SRS DS345) was used to drive the QTFs into resonance. The electrical outputs from the QTFs due to the resonance were amplified with a current amplifier and then sent to a lock-in amplifier (Stanford Research Systems SRS SR830). To drive all the QTFs in an array, we linearly swept the frequency of the AC modulation within a range that covers the resonance frequencies of all the QTFs. The output from the lock-in amplifier was recorded as a function of frequency with a digital oscilloscope of 12-bit resolution (Yokogawa) to provide a spectrum of the entire array. All measurements were carried out at room temperature, (22.7 ± 0.5) °C.

Polymers. Ethylcellulose polymers (Aqualon EC) and butylcellulose (Butyl) were donated by Hercules Incorporated Aqualon Division (Wilmington, DE) and Custom Shielding (Gilbert, AZ), respectively. The hydrophilicity or hydrophobicity of the EC polymers can be adjusted with different degrees of substitution (SD). The EC polymers used in this work are T-10 (SD = 50.6%), N-22 (SD = 49.0%), and N-7 (SD = 48.5%). Apiezon wax made of high molecular weight petroleum hydrocarbons (Apiezon wax) was purchased from (Apiezon, Ringoes, NJ). The wax, T-10 EC, and butylcellulose were dissolved in toluene; N-22 EC and N-7 EC were dissolved in absolute ethanol. Poly(vinylphosphonic acid) (pvpa) (Polysciences, Inc.) and poly(acrylic acid) (paa) (Sigma, molecular weight: 250 000) solutions were prepared in deionized water. Commercial polymer mixtures, transparent nail polish (Nailslicks, Noxell Corp., Hunt Valley, MD) and Super Glue (Duro, TM of Henkel Loctite Corp.) were used as received.

Formation of Polymer Wires. The polymer wires were formed at room temperature by pulling the polymer gels or viscous solutions according to the following procedure.²⁵ First, two small drops (0.1–1 μ L) of a polymer solution containing a few tens of polymer nanograms were placed on both QTF prongs. Before the drops completely dried out, a hypothermic syringe needle was dipped into one of the polymer drops and pulled into the drop of the second prong (Scheme 1A).²⁵ The pulling dragged a strand of polymer solution across the gap between the two prongs. The surface tension on the strand led to capillary thinning and formation of a thin polymer wire (Scheme 1B). The diameter of a typical polymer wire is between a few hundred nanometers

to a few micrometers. The polymer wires were left in air to dry out overnight before use.

Coating QTF with Polymers. In addition to bridging the QTF prongs with polymer wires, an alternative way to use polymers as sensor materials is to coat the QTFs with a thin layer of polymers.²³ We have also tried this method by placing a drop (<0.35 μ L) of dilute polymer solutions on the surface of the prongs. The deposited mass of the polymers was a few tens of nanograms in all cases. This method reduces the sensitivity, but it is useful for those polymers that cannot be easily stretched into thin wires. As we will discuss later, QTFs coated with proper polymer thin films are particularly good for monitoring relative humidity, which does not require high sensitivity.

Relative Humidity Detection. Saturated solutions of MgCl₂, NaBr, NaCl, and deionized water were used to control the relative humidity at 33, 58, 75, and 100%, respectively. A QTF coated with 23.8 ng of pvpa (0.35 μ L of 34 ng/ μ L pvpa solution on each prong) was used as a humidity sensor. The pvpa-coated QTF was placed in a sealed chamber with a humidity controlled by one of the above-mentioned saturated salt solutions.

***p*-Nitroethyltoluene and Ethanol Detection.** Various concentrations of *p*-nitroethyltoluene and ethanol detection vapors were prepared by mixing proper amounts (varying from few microliters to 0.3 mL) of saturated *p*-nitroethyltoluene or ethanol vapor with 65 mL of air at room temperature. The air relative humidity was monitored with a commercial humidity sensor (Taylor). The vapor at each concentration was then introduced into a 6-mL sample chamber in which a QTF array was mounted (see Supporting Information for more details). No significant differences in the resonant frequency changes were observed when 65-mL injections were performed on the same sensor array using a 6-mL or a 60-mL cell. For this reason, a ratio sample volume/cell volume of 10 was high enough to exchange the sample mixture in the chamber.

Analysis of beer vapors. Alcohol concentrations (%/vol) of commercial beers were determined by placing a QTF array 1 cm from a 300- μ L portion of beer in a cup. The cup and the QTF sensor array were placed in an open 20-mL syringe, and the resonance spectra of the QTF array were recorded before and after exposure to the beer vapors (see Supporting Information for more details).

RESULTS AND DISCUSSION

Relative Humidity (RH) Sensor. Figure 2A shows the spectrum of a QTF array, consisting of a bare QTF, a pvpa-, and a butylcellulose (butyl)-coated QTF at 42% RH. The resonance frequencies of the polymer-coated QTFs are lower than that of the bare fork due to increased mass. The quality factors (Q) of the all three QTFs are about 8000, which shows that the coating does not affect Q significantly. Figure 2B shows the response of the QTF array to the injection of saturated water vapor (100%) at a flow rate of 1 mL s⁻¹ into a 6-mL cell. A -0.15 -Hz maximum frequency shift was observed for the bare and the butyl-coated QTFs, whereas a much bigger response (-24.69 Hz) was detected for the pvpa-coated QTF. The sharp difference is because butyl is insoluble in water and pvpa is very hydrophilic.²⁶ Note that the

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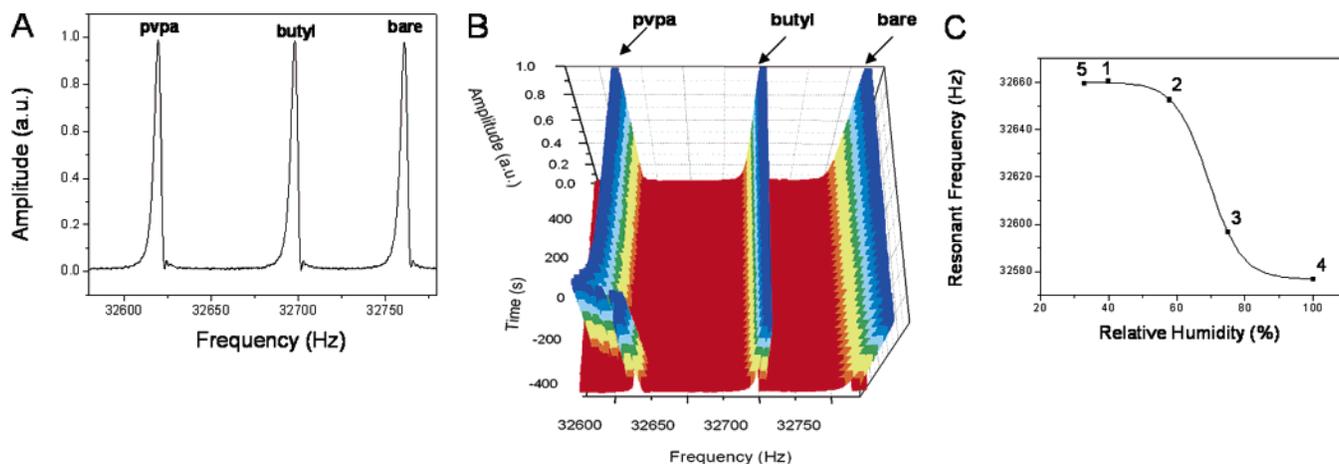


Figure 2. (A) Oscillation amplitude vs frequency plot for a QTF array of a bare QTF and coating film QTFs modified with pvpa and butylcellulose (Butyl). (B) Time course of the oscillation amplitude vs frequency plot upon the injection of 65 mL of saturated water vapor (100%) at a flow rate of 1 mL s⁻¹ into a 6-mL cell. (C) Resonance frequency shift vs relative humidity (RH). The numbers indicate the order of tested RH. The solid line is a guide to the eye. The coating film was made by placing ~0.35 μL of 34 ng μL⁻¹ pvpa solution on each QTF prong and overnight drying at room temperature.

maximum frequency shift was obtained at the end of the injection. When the injection was off, the resonant frequency increased due to a partial gas leak from the chamber. After the injection of water vapor, we opened the chamber to reexpose the QTF array to the ambient air and found that the resonance frequency of the pvpa-coated QTF returned to the initial value after 10 min.

We also studied the response of other widely known hydrophilic polymers, such as poly(acrylic acid), poly(acrylamide), poly(styrene sulfonate), to water vapor. Although, they are all sensitive to water vapor, poly(vinylphosphonic acid) is the most sensitive to RH changes. For this reason, we determined the response of the pvpa-coated QTF as a function of RH. Figure 2C plots the frequency shift vs RH, which follows a sigmoid behavior. The numbers marked in the figure indicate the order of the test. We increased the RH (starting from "1") and lowered the RH (ending at "5") and found that the response was fully recoverable within 5 min. Using the plot shown in Figure 2C as a calibration curve, we determined RH in the following 7 days, and the results were in good agreement with the readings of the commercial RH sensor.

For comparison, we tested the ability of the pvpa-wire-modified QTF for RH detection and found that it was too sensitive and broke when RH was >26%. Below 26% RH, the resonance frequency of the pvpa-wire-modified QTF shifted by several hundred hertz upon a small RH increase. These comparative studies showed that the pvpa-coated QTF is good enough to meet the need for RH monitoring, but the polymer-wire-modified QTFs are the choice for applications that require high sensitivity.

Detection of *p*-Nitroethylbenzene Vapors. To demonstrate the ability of the polymer wire QTFs for detecting low-concentration chemical vapors, the first example that we have studied is *p*-nitroethylbenzene (NEBz), an ethylbenzene (EBz) derivative found in petroleum. EBz is a serious environmental pollutant released into the air from automobiles and the chemical industry, and NEBz is an atmospheric product from the combination of EBz and nitrogen oxides.²⁷ The detection of both aromatic compounds is important from an environmental and health point of view.

Implementation of simple techniques for NBz derivatives detection in the parts-per-billion range is essential for air quality control.²⁷

Since NEBz is a hydrophobic molecule, we chose different hydrophobic polymers as the sensing wires: polystyrene, Parafilm, and Apiezon wax. We found that the wax, a mixture of 62% paraffinic hydrocarbon polymer and 38% asphaltene hydrocarbons,²⁸ was the most appropriate choice to detect NEBz because of its chemical and mechanical properties. To optimize the sensitivity, we varied the dimensions of the polymer wire using eq 1 as guidance.²² The equation relates the relative frequency shift ($\Delta f_0/f_0$) to the length (L) and cross-sectional area (A) of the wire, the chemical binding induced change in the Young's modulus (ΔE), and the effective spring constant of the QTF (k_{fork}).

$$\frac{\Delta f_0}{f_0} \cong \frac{A}{2Lk_{\text{fork}}} \Delta E \quad (1)$$

According to the equation, for a given ΔE , short and thick wire generates a larger frequency shift and, thus, a higher sensitivity. However, a thick wire means that the analytes have to diffuse over a longer distance into the wire, which slows down the response time. Thick wires may also introduce more damping and lower the quality factor, which affects accurate determination of the resonance frequency. We have found that the best way to combine sensitivity and response time is to shorten the length as well as decrease the wire thickness.

Figure 3A shows the response of a wax wire QTF upon the injection of 100 ppb NEBz at 1.5 mL/s. The resonance frequency decreases immediately and reaches a minimum at the end of the injection. After the injection, the resonance frequency started to increase because a partial gas leak in the chamber and recovered the initial value after the chamber was purged with N₂ for ~30 min. In principle, the adsorption of organic vapors can change both the mass and the spring constant of the polymer wire. To determine the relative importance of the two effects, we

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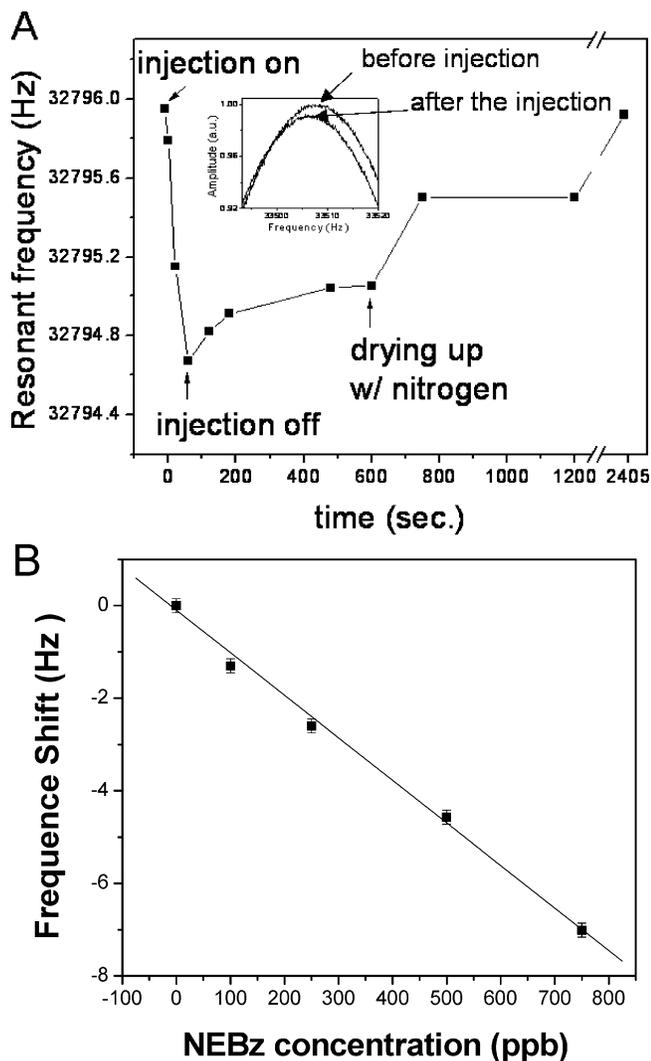


Figure 3. (A) Time course of the resonant frequency of a wax wire ($\sim 20 \mu\text{m}$)-modified QTF during the injection of 65 mL of 100 ppb NEBz and then purging with N_2 . Inset: oscillation amplitude vs frequency plot before and at the end of the NEBz injection. (B) Wax QTF resonance frequency shift as a function of NEBz concentration.

tested a broken polymer wire and found no significant change in the resonance frequency within the experimental error ($\sim 0.2 \text{ Hz}$) in the presence of NEBz. This control experiment clearly demonstrated that the change in the spring constant is far more dominant than that of the mass increase. It is also consistent with the humidity detection discussed above, which shows the pypa wire QTF is much more sensitive to humidity than the pypa film-coated QTF.

The wax wire QTF can also discriminate NEBz from other common chemical vapors, such as water, ethanol, and acetone. We have performed the experiment in the presence of water, ethanol, and acetone vapors and did not observe interference of these vapors with the detection of NEBz (not shown). The sensitive dependence of the effective spring constant of the polymer wire on the organic vapors can be understood on the basis of the following considerations. When the polymer is pulled into a wire, the individual polymer chains are forced to align along the pulling direction through capillary forces²⁵ (Scheme 1B). After the organic solvent is evaporated, the polymer chains are trapped

in this configuration via noncovalent interactions with the neighboring polymer chains. When the wire is exposed to an organic vapor, the organic molecules penetrate into the wire and “redissolve” the polymer chains, thus softening the polymer wire²² (Scheme 1B). In the case of NEBz detection with wax wires, the analyte is an aromatic compound that can easily dissolve the petroleum derivative wax, which contains a high percentage of asphaltene hydrocarbons (36%).

The resonance peaks of a wax wire QTF (different from that shown in Figure 3A) before and after exposure to 100 ppb NEBz is shown in the inset of Figure 3A. By fitting such resonance peaks with Lorentzian functions, the NEBz-induced resonance frequency shift can be accurately determined. The typical uncertainty in the fitted curves is 0.02 Hz or even lower. The maximum standard deviation (SD) from control experiments was 0.15 Hz, which leads to a detection limit (defined on a signal equal to 3SD) of a few tens of parts per billion. This detection is in the range of that required to monitor petroleum derivatives in air.²⁷ Additionally, the same polymer material used under the same wire production conditions generated wires with similar responses (Figure 3A including inset). Figure 3B is a calibration plot of the resonance frequency shift of the wax wire QTF vs the NEBz concentration, which shows a linear dependence response.

We note that the polymer wire QTF is rather stable in an ambient environment and can be repeatedly used without degradation for at least 2 months (tested so far). The high stability is due in part to the extremely high stability of the quartz tuning forks and the wax wire in air, even in the presence of high humidity.

Detection of Ethanol Vapors. Detection of polar chemical vapors, such as ethanol, is considerably more challenging than that of nonpolar chemicals, because of the interference of large amount of water vapor in ambient air. We attempted to solve this problem by using an array of QTFs, consisting of one devoted to monitor relative humidity and several others made of polymers with different affinities to the chemical vapor. Figure 4A shows the spectrum of an array of four QTFs, wax, nail polish (NP), and Super Glue (SG) (both mixtures of hydrophilic and hydrophobic substances) and poly(acrylic acid) (paa). These polymers vary from highly hydrophobic wax to highly hydrophilic paa. Attachment of these polymer wires to the bare QTFs increased the resonance frequencies by different amounts, which allowed us to separate the four polymer wire QTFs in the spectrum. The Q values of the polymer wire QTFs are ~ 1500 , ~ 3000 , ~ 1500 , and ~ 1000 for wax, paa, NP, and SG, respectively.

We studied the response of this QTF array to ethanol vapor of different concentrations. With the exception of the wax wire QTF that does not respond to ethanol vapor, the other three, paa, NP, and SG, can all provide a parts-per-billion level of detection of ethanol vapor, but the response depends on the humidity of the air.²⁹ This led us to determine the calibration curves of the QTFs at different RHs (Figure 4B–D). At a given RH, the frequency increases exponentially with the ethanol concentration, but the frequency response increases with RH. This RH-dependent effect is strongest for paa, which is the most hydrophilic polymer (Figure 4B). The increased frequency response to ethanol at high RHs shows that water adsorbed in the polymer wire from humid

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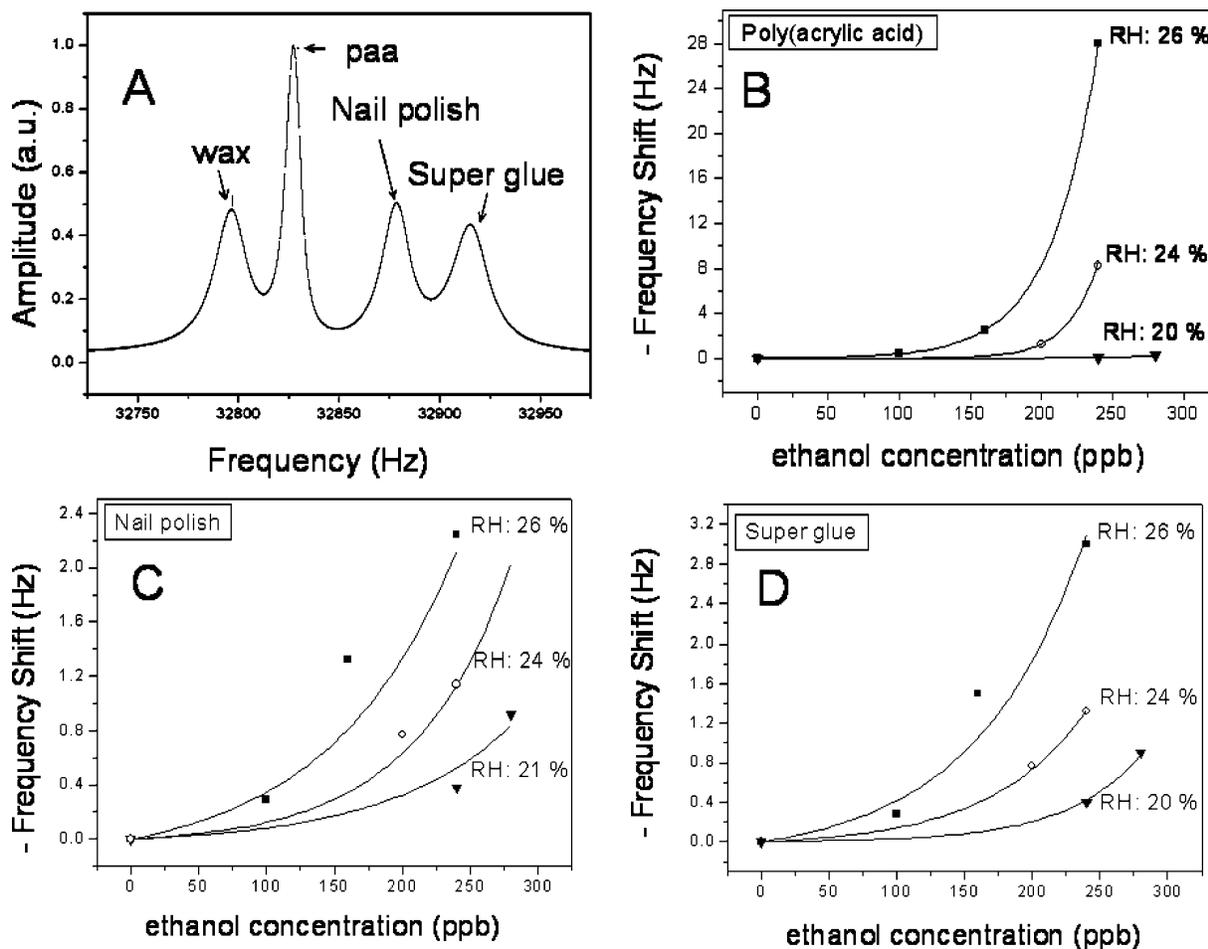


Figure 4. Polymer wire QTF array made of wax, poly(acrylic acid) (paa), nail polish (NP), and Super Glue (SG). (A) Oscillation amplitude vs frequency plot at 26% RH. Resonance frequency shift as a function of ethanol concentration at 20, 24, and 26% RH on (B) paa, (C) NP, and (D) SG wire TF.

air enhances the capability of the wire to adsorb ethanol vapor, which can be attributed to the strong affinity of ethanol to water.²⁹

Since ethanol is an ambivalent molecule (can dissolve in both water due to its hydroxyl group but also in hydrophobic solvents due to its nonpolar hydrocarbon groups), we decided to test more hydrophobic polymers in order to minimize RH interference. Ethylcellulose (EC) is a good candidate for this test because its degree of hydrophilicity/hydrophobicity can be controlled through the degree of substitution of ethoxyl groups per anhydroglucose unit (Figure 5A).²⁶ We built a polymer wire QTF array using ECs with different degrees of substitution, EC T-10 (50.6%), EC N-22 (49.0%), and EC N-7 (48.5%). We also included a pvpa-coated QTF in the array as an internal calibration of RH. The spectrum of the array is plotted in Figure 5B. The individual resonance peaks in the spectrum were well-defined, with Q values varying between 830 and 1100.

We tested the solubility of the ECs in water and in absolute ethanol. None of the ECs appeared to be soluble in water, EC N-22 and EC N-7 were fully soluble in ethanol, and EC T-10 was partially soluble in ethanol. Figure 5C shows the frequency shifts of the QTFs upon exposure to 65 mL of ethanol mixtures at 1.5 mL s^{-1} at 35–37% RH. The most hydrophobic polymer, EC T-10, gave the largest frequency shift, with a sensitivity of $\sim 3 \times 10^{-3} \text{ Hz per ppb}$ of ethanol. The EC N-22 wire QTF was the

second most sensitive, with sigmoid response-concentration dependence, and EC N-7 was least sensitive to ethanol. The pvpa-coated QTF did not show any concentration-dependent response to ethanol, which serves as a good calibration standard for RH. The data shown in Figure 5C were taken with an ambient RH between 35 and 37%. We performed a blind test in which the unknown concentrations of ethanol vapors prepared by one of the authors were tested by another. One example of such test is shown in Figure 5C. In all cases, the QTF sensor can determine the ethanol concentrations with an error $\sim 15\%$.

The frequency responses of the EC wire QTFs were not as sensitive to RH as the paa, NP, and SG wires shown in Figure 4B–D, which is because these EC polymers are not soluble in water. However, very high RH does affect the frequency response. To achieve a better understanding of the RH effect, we tested mixed ethanol–water vapor of different ratios. Figure 6A–C shows the frequency shift vs ethanol concentration with 36 and 100% water vapors. Since higher humidity shifts the resonance frequencies even without the presence of ethanol vapor, we normalized the frequency shift with the frequency shift without ethanol. The plots show that 100% water vapor lowers the sensitivity of T10 for ethanol detection and makes N-7 and N-22 essentially insensitive to ethanol. These results show the importance of monitoring RH in order to accurately determine ethanol vapor concentrations.

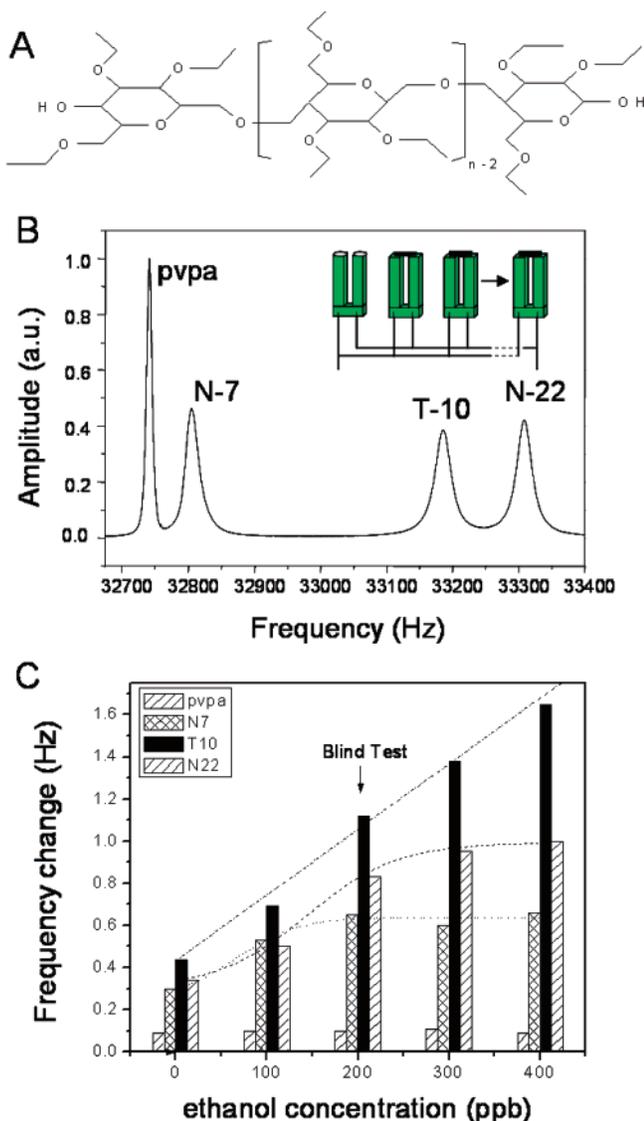


Figure 5. (A) Structure of ethylcellulose (EC) with complete (54.88%) ethoxyl substitution. (B) Oscillation amplitude vs frequency plot for an array of QTFs modified with pvpa coating, N-7, T-10, and N-22 EC wires, respectively. (C) Negative resonance frequency change as a function of ethanol concentration obtained from the QTF array in (B) at 35–37% RH. The solid lines serve as guides to the eye.

Interactions between ethanol and water²⁹ in gas phase seem to play an important role and determine the sensitivity of the sensor array toward ethanol vapors at high RH.

Analysis of Ethanol Percentage of Beers. To further demonstrate the performance of the QTF sensor array, we tested the vapors of several commercial beers. We first determined calibration curves by exposing the EC wire QTF array for 10 min to 300 μ L of beers with known ethanol concentrations placed 1 cm away in an open air environment (37–38% RH). As a control experiment, we also tested the vapor of 300 μ L of water under the same conditions (marked as 0%/vol in Figure 7). The frequency response of the array vs ethanol concentration is plotted in Figure 7, which shows clearly that the frequency shift increases with the ethanol concentration. Using the plot in Figure 7 as calibration curves, we determined the ethanol concentration of unlabeled commercial beers. For example, we determined Bud

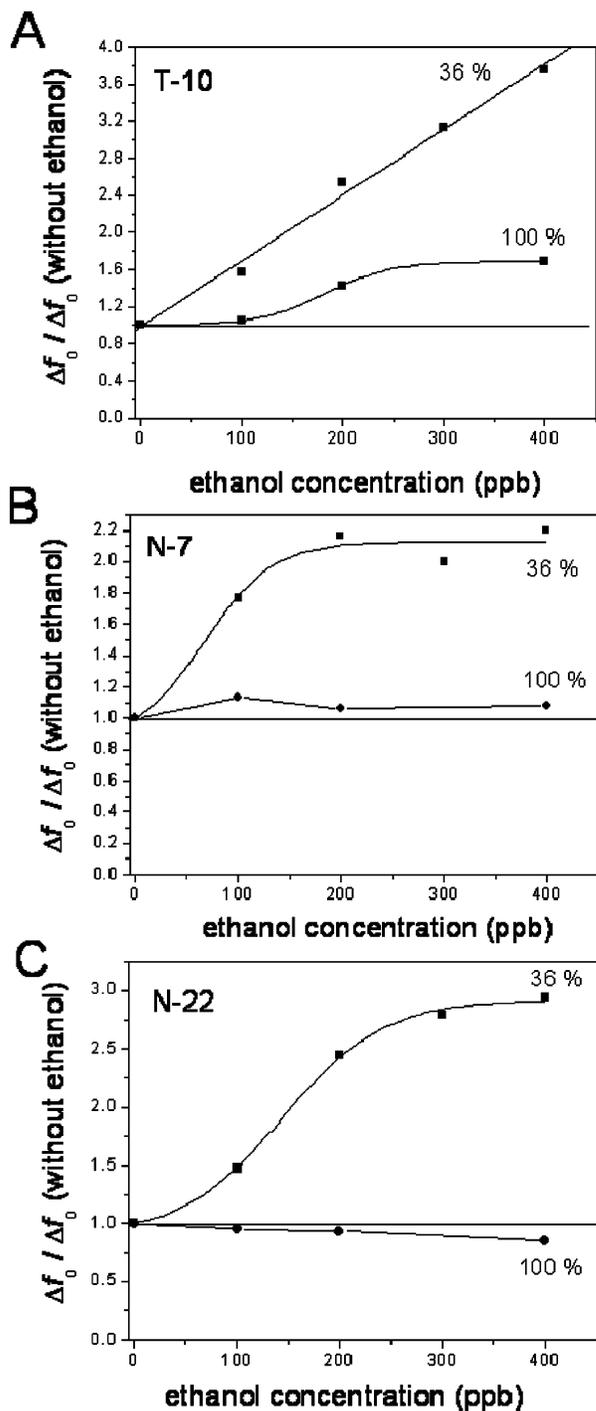


Figure 6. Normalized frequency shift of the pvpa-ECs QTF array [$\Delta f_0 / \Delta f_0$ (without ethanol)] as a function of ethanol concentrations obtained at different RHs.

Light ethanol concentration to be 3.4%, which agrees with the declared concentration on the website.³⁰

CONCLUSIONS

We have demonstrated a simple, low-cost, and miniaturized chemical vapor sensor using wristwatch QTFs. An array of such QTFs, each with a polymer microwire stretched across its two prongs, provides sensitively and rapid detection of chemical

(30) <http://www.nd.edu/~ucc/bac.html>.

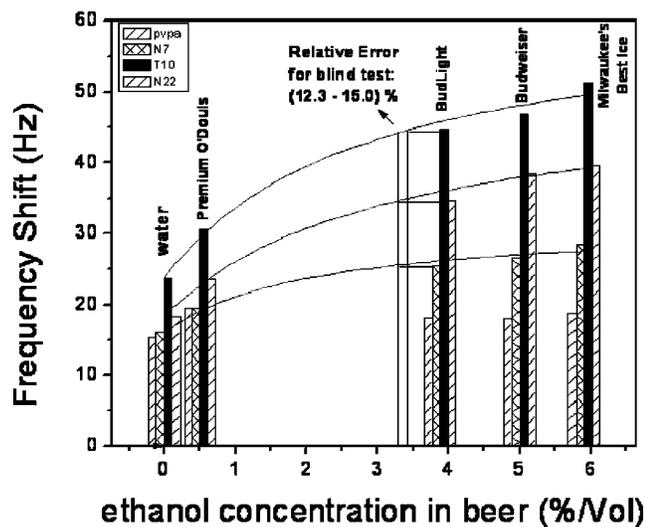


Figure 7. Negative frequency responses of the ECs—pvpa QTF sensor array to the vapors of various commercial beers under ambient conditions. The solid lines serve as guides to the eye.

vapors. The selectivity of such a sensor is based on proper selection of the polymers and also on the frequency response pattern of the QTF array. For nonpolar vapors, the interference due to large amount of water vapor (RH) in ambient air can be reduced to a minimum by using highly hydrophobic polymers;

however, the RH interference is much harder to remove completely in the case of polar vapor (ethanol) detections. We found that the most effective way to solve this interference problem is to calibrate the sensor response at different RHs and to use the calibration curve to determine analyte concentration once the RH is known. To monitor RH, we included a QTF humidity sensor into the array. Using the QTF sensor arrays, we have detected the presence of small amounts (<100 ppb) of NEBz, ethanol (~100 ppb), and ethanol in commercial beers.

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SUPPORTING INFORMATION AVAILABLE

Supporting information as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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