Chapter 2

Gas Sensing Ionic Liquids on Quartz Crystal Microbalance

Yi-Pin Chang and Yen-Ho Chu

Additional information is available at the end of the chapter

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Abstract

Recent advances in "designer solvents" have facilitated the development of ultrasensitive gas sensing ionic liquids (SILs) based on quartz crystal microbalance (QCM) that can real-time detect and discriminate volatile molecules. The amalgamation of tailored-made SILs and label-free QCM resulted in a new class of qualitative and semi-quantitative gas sensing device, which represents a model system of electronic nose. Because a myriad of human-made or naturally occurring volatile organic compounds (VOCs) are of great interest in many areas, several functional SILs have been designed to detect gaseous aldehyde, ketone, amine and azide molecules chemoselectively in our laboratory. The versatility of this platform lies in the selective capture of volatile compounds by thin-coated reactive SILs on QCM at room temperature. Notably, the detection limit of the prototype system can be as low as single-digit parts-per-billion. This chapter briefly introduces some conventional gas sensing approaches and collates recent research results in the integration of SILs and QCM and finally gives an account of the state-of-the-art gas sensing technology.

Keywords: chemoselective gas sensing, ionic liquid, label-free detection, quartz crystal microbalance and volatile organic compound

1. Introduction

Real-time detection and monitoring of naturally occurring or human-made volatile compounds are of paramount importance in many areas such as (1) disease diagnosis (e.g., breath VOCs); (2) manufacturing industry (e.g., flammable and toxic gases); (3) environmental protection (e.g., automobile emissions and greenhouse gases); (4) indoor air quality monitoring (e.g., asphyxiant and hazardous gases); (5) homeland security (e.g., chemical and biological warfare agents). Mammalian olfaction has been used as tools in many settings to detect or measure

volatile molecules in drinks, food, perfumes as well as explosives and illegal drugs. Perfumers, flavorists and sniffer dogs are trained professionals and experts in aroma; however, they cannot work 24/7 and their sensory can be extremely subjective, regardless of other factors such as sensitivity, toxicity and when sites are beyond reach. Inspired by the mammalian olfactory system, artificial olfaction or electronic noses have been developed to precisely analyze smells or odorants [1]. In this chapter, the development of chemoselective SIL-based QCM gas analysis system for the detection of VOCs in our laboratory is described. **Figure 1** illustrates the side-by-side comparison of the human olfactory system and the SIL on QCM gas sensing system.

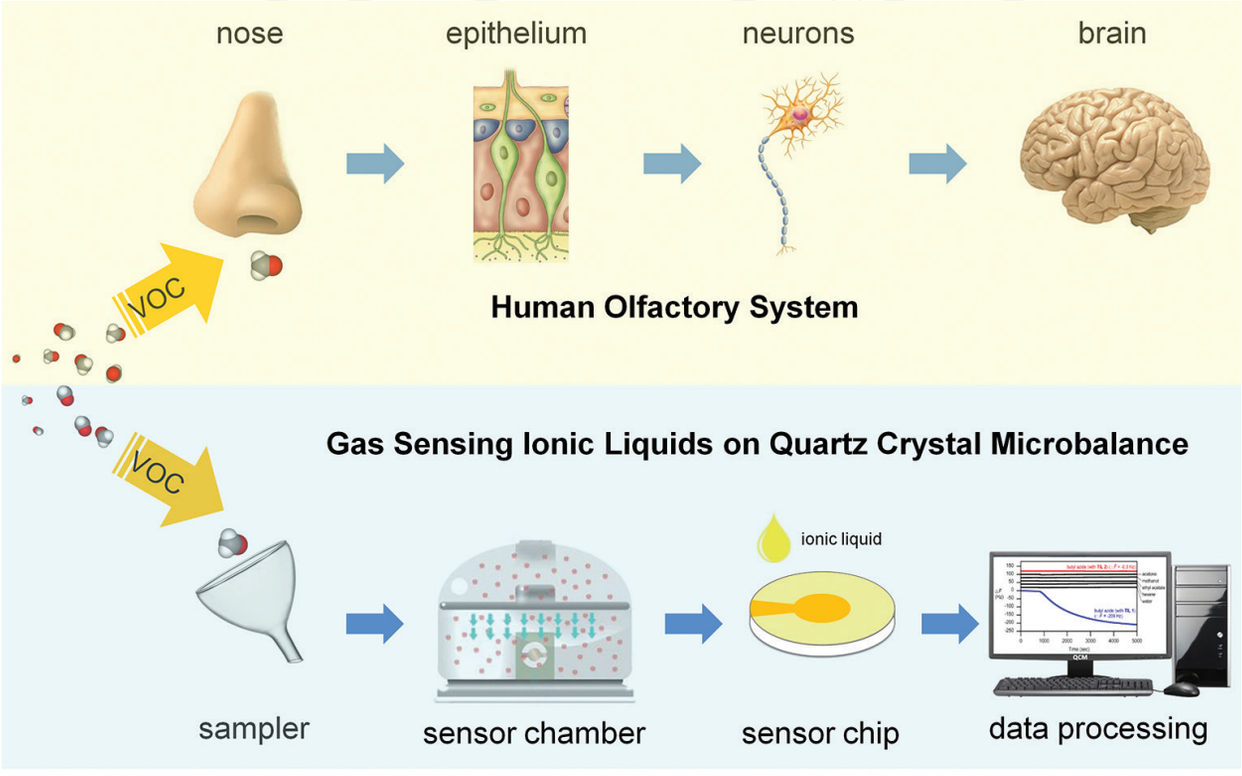

Figure 1. Side-by-side comparison of the human olfactory system and the SIL on QCM gas sensing system.

Gas is one of the fundamental states of matter that is considered between the liquid and plasma states. Unlike other states of matter, what distinguishes gas from liquid and solid is the distinct separation of the individual gas molecules, which makes them travel fast and freely, and is usually invisible to the human naked eyes. A pure gas can be composed of single atoms (e.g., noble gas), one type of atom (e.g., oxygen), or organic molecules made from a combination of atoms (e.g., acetone). The question is how to selectively detect and precisely measure a single gas out of a mixture of other gases? In the human olfactory system, volatile compounds are inhaled into nasal cavity and then diffuse through mucus to epithelium receptor cells. The peripheral system then senses the external stimulus and the central system encodes it as an electric signal in neurons, where all signals are integrated and processed in the brain to give us the sense of a smell. The design of a gas sensing device is similar to human

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olfaction, in which the sensing material plays a pivotal role in the recognition or capture of volatile molecules. The gas sample passes through the sensor chip and induces physical or chemical changes in the sensing material, which are transduced into electrical signals or patterns and then processed by a computer system. The sensing material should be sensitive enough to recognize the presence of target gas, which is the counterpart of the peripheral system in the human olfactory system. The first event of molecular recognition underscores the importance of sensing material that sensitivity and selectivity are inherited in the gas sensing system.

Ionic liquids are room-temperature molten salts that have been increasingly used in electrochemical devices, such as batteries, fuel cells and biosensors. Their intrinsic unique physiochemical properties by design have facilitated the birth of a variety of novel sensing technologies in recent years. Zhang et al. [2] reported fabrication of polymeric ionic liquid/graphene nanocomposite for glucose oxidase immobilization and direct electrochemistry. Liu et al. described a hydrophobic ionic liquid was used as an entrapping agent to facilitate the electron transfer of horseradish peroxidase on a glassy carbon electrode [3]. Ratel et al. developed imidazolium-based ionic liquid self-assembled monolayers for binding streptavidin to promote affinity biosensing [4]. Abdelhamid et al. designed UV-light absorbing ionic liquid matrices for matrix-assisted laser desorption/ionization mass spectrometry (MS) [5]. Arkan et al. demonstrated an impedimetric immunosensor based on a gold nanoparticle/multiwall carbon nanotube-ionic liquid electrode for the determination of human epidermal growth factor receptor 2 [6]. As shown above, the scope of the applications of ionic liquid-based sensors is abundant, but its use in gas sensing is in the ascendant.

Conventional gas sensing methods can be generally categorized into conductivity sensors (e.g., metal-oxide semiconductors and conducting organic polymers), piezoelectric sensors (e.g., quartz crystal microbalance (QCM) and surface acoustic waves (SAW) and spectroscopic instruments. These gas sensing systems require a set of reactive materials that recognize gaseous molecules and transduce the volatile compounds into electrical signals. A number of nanomaterials have been developed for gas sensing, such as field effect transistors (FETs) based on single-walled carbon nanotubes (CNTs) [7, 8]. The design of sensing materials generally utilizes the "lock-and-key" method, which has theoretical high sensitivity and selectivity. In some cases, it may not be practical for the analysis of complex samples due to the fact that most sensing materials exhibit some cross-reactivity to structurally similar compounds. In addition, higher selectivity may come at the price of irreversibility, lengthy recovery times, memory effects and lower sensitivity (detection limits down to hundreds part-per billion).

QCM is a highly sensitive instrument that measures the mass difference per unit area by recording the change in resonant frequency of a build-in quartz crystal [9]. The transduced signal (ΔF) represents the measured frequency change (Hz), which is based on a physical phenomenon called the converse piezoelectric effect. Piezoelectricity is generated on opposite surfaces of a crystalline material upon mechanical deformation (e.g., pressure or torsion) of the crystal along a given direction. Among the many types of crystals exhibit piezoelectricity, quartz exceptionally possesses the desired chemical, electrical, mechanical and thermal

properties and is thus used as the crystal in QCM systems. In order to make the best use of QCM, exquisite design on the chip is needed to functionalize the electrode with a variety of surface chemistries and modifications for molecular recognition [10]. Our laboratory has a long-standing interest in QCM, where a 9-MHz QCM apparatus was used to develop the integrated system equipped with ionic liquids tailored for reaction-based gas sensing. This chapter will give a brief introduction on current gas sensing technologies and latest advances in the field of gas SILs based on QCM.

2. Gas sensing methods

2.1. Spectroscopic gas sensors

Spectroscopic instruments are mainly based on absorption and emission spectrometry. The principal of absorption spectrometry is the Beer Lambert law that differential optical absorption spectroscopy, Raman light detection and ranging, tunable diode laser absorption spectroscopy, and so on, have been developed. One of the most commonly used on-site methods for continuous monitoring of airborne VOCs is differential optical absorption spectroscopy [11]. It has the advantages of fast response time and low limit of detection, but also has the disadvantage of optical interference from oxygen, ozone, and several hydrocarbons. The theory of emission spectrometry is that excited atoms emit photons and then return to its ground state that laser-induced breakdown spectroscopy is one example. Interestingly, Fourier transform infrared spectroscopy can be used in either absorption or emission spectrometry such as non-dispersive infrared and quantum-cascade lasers gas sensors for the latter [12].

Analytical instruments have been utilized for gas detection such as mass spectrometry (MS) and gas chromatography (GC). Mass spectrometry via direct injection is frequently used for the detection of VOCs. To enhance the sensitivity required for the identification of trace levels of VOCs, tandem mass analysis is typically employed. Ions of a particular mass to charge ratio are selected first and then subject to the next stage for further fragmentation. The fragmented daughter ions are analyzed without interference of large amount of unrelated parent fragments and thus beneficial for the detection of trace gases in complex mixtures. For example, Proton-transfer reaction mass spectrometry (PTR-MS) is among the techniques that have been used extensively for on-line analysis of VOCs [13]. The PTR-MS technique offers rapid and accurate measurement of VOCs with a very low limit of detection. However, isomeric and isobaric compounds are not able to be separated and measured individually by PTR-MS instruments. On the other hand, gas chromatography (GC) in conjunction with flame ionization detection, mass spectrometry or photoionization has been utilized for VOC detection such as in the food industry [14]. GC is used for analyte separation, while the coupled detector is for the measurement of separated analyte. These GC-related methods normally utilize batch detection that involves analyte sampling, transportation, pre-concentration and finally separation via chromatography before data analysis. These methods are useful for trace VOC detection, but they are time- and labor-consuming. In addition, the concentration detected

from such analysis is the average or accumulated level rather than spatial variations over the sampling time period.

2.2. Conductivity gas sensors

Metal-oxide (SnO_2, CuO, Cr_2O_3, V_2O_5, WO_3 and TiO_2) semiconductors are one of the most common sensing materials due to its low cost and good sensitivity [15, 16]. The principle of detection is through redox reactions between the oxide surface and the target gas, where the electronic variation on the oxide surface is transduced into an electrical resistance variation. Depending on the transducer, the difference of resistance can be determined by the change of capacitance, mass, optical characteristics, reaction energy or work function. Metal oxides have been used to detect combustible, oxidizing, or reducing gases such as carbon monoxide, hydrogen, liquid petroleum gas, methane and nitrogen oxide [17]. Despite the fact that some metal-oxide semiconductors have good sensitivity, they may also suffer from poor response linearity and selectivity due to the interference of other gases. In addition, most metal-oxide gas sensors require high operating temperature (up to 500 °C) to reach the optimal reaction temperature for the target gas [18]. The sensing material has to be preheated to enhance the adsorption of gas molecules on the sensing surface, which has limited the application of metal-oxide gas sensors. Another major issue is the long recovery time that may make it unpractical for the development of electronic noses. In general, metal-oxide gas sensors exhibit drastically greater sensitivity to inorganic gases and a few VOCs such as ethanol and formaldehyde. However, it has been demonstrated that the indiscriminate response of methyl, ethyl, isopropyl and butyl alcohols on SnO_2 films, which reflects the major challenges in gas sensing using metal-oxide semiconductor devices, that is, selectivity and response time. In addition, many other VOCs that result in health problems are not able to be detected by metal-oxide gas sensors effectively [19].

On the contrary, conducting polymer-based gas sensors are frequently used to detect a wide range of gases such as VOCs, aromatic volatiles and halogenated compounds. The organic gas sensing polymer composite may be spray-, spin-, or dip-coated onto the sensor, which typically has two electrodes that are fabricated on an insulating polymer. Upon exposure to a gas, the physical properties of the insulating substrate changes due to the absorption of volatile molecules. The signal transduction mechanism can be described by London dispersion, dipole/induced dipole interactions, dipole/dipole interactions and hydrogen bonds, in which responses are normally measured as the relative differential resistance. Polyaniline, polypyrrole, polythiophene and their derivatives are typical organic conducting polymers that have been investigated for gas sensing, in which doping process is required to increase conductivity by redox reactions or protonation [20]. Polymer-based gas sensors have several advantages for gas detection, including high sensitivity and short response time. Moreover, while operation temperatures of metal-oxide gas sensors are usually more demanding, polymer-based sensors operate at room temperature. However, polymer composites are also sensitive to temperature fluctuations that may result in variation of sensor responses and thus output errors in the system.

2.3. Piezoelectric sensors

A general piezoelectric gas sensor is composed of a substrate of quartz that is cut at a crystalline angle to support a pressure- or mass-sensitive material that is coated on the quartz surface. QCM and surface acoustic wave (SAW) devices are two typical microbalance sensors that the former employs a bulk acoustic wave sensor while the latter uses a surface acoustic wave sensor. Sensing materials such as non-conducting polymers can be coated on QCM and SAW sensors to detect the analytes of interest. When the sensing material adsorbs specific molecules, the mass of the coated material increases and causes the acoustic waves to travel slower. The piezoelectric quartz converts acoustic waves to electric signals. This subtle change in mass can be detected by the sensor microelectronics once the acoustic wave is converted to an electric signal. The signal response varies in physisorption and chemisorptions. A few materials such as carbon nanotubes [21], ionic liquids [22] and molecular imprinted polymers [23] have been used to coat on QCM and have enabled the detection of a variety of pollutants and the sensing of VOCs. Temperature and humidity control are the major issues for accurate detection, as the resonant frequency is affected by those factors in this type of gas sensors. Therefore, modifications in coating materials have been the focus to improve the sensitivity and specificity in gas sensing. Some commercial QCM sensor systems are available for moisture and inorganic gas detection, but the detection for VOCs is rare and sensitivity is typically in the range of 10–103 ppm, which is not good enough for trace level detection [24].

3. Gas sensing ionic liquids and quartz crystal microbalance

3.1. Ionic liquids for gas sensing

A sensor array using room-temperature ionic liquids as sensing materials and a QCM as a transducer was developed for the detection of ethanol, dichloromethane, benzene and heptane at ambient and elevated temperatures [25]. These ionic liquids responded proportionately and reversibly to the volatile compounds at room and elevated temperatures but deviated from this linear relationship at high concentrations for the highly volatile dichloromethane. The different response intensity of the gas sensor to the volatile compounds depends on the solubilities of organic vapors in ionic liquids and interactions between each organic vapor and ionic liquid. In addition, the study of a diverse set of ionic liquid showed structural differences resulted in selective responses. Consequently, a sensor array of ionic liquids is promising to effectively differentiate different volatile compounds in pattern recognition in room or high temperatures. A room-temperature ionic liquid has also been developed for the sensing of ammonia gas. The work function responses of the cast films with and without IL were analyzed by "stepwise" changes of ammonia gas concentration from 0.5 to 694 ppm in air. The camphorsulfonic acid-doped polyaniline layers showed enhanced sensitivities, lower detection limits and shorter response times. Experimental evidence suggested that polyaniline forms a charge-transfer complex with imidazolium cation [26]. The first use of ionic liquid-doped electrospun nanofibrous materials as highly responsive fluorescence quenching-based optical CO_2 sensors was reported. The sensor slides have high sensitivities due

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to the high surface area-to-volume ratio of the nanofibrous membrane structures. The preliminary results showed that the sensitivities of electrospun nanofibrous membranes to detect CO_2 are 24- to 120-fold higher than those of the thin film-based sensors. The response times of the sensing reagents were short, and the signal changes were also fully reversible. In addition, the stability of the employed matrix materials was excellent as there was no significant drift in signal intensity after stored in the ambient air for months [27]. The effects of conductive polymer oxidation states and structures on the design and development of ionic liquid/conductive polymer composite films for gas sensing have also been systematically characterized. Polyvinyl ferrocene films were tested for their sensing properties (e.g., sensitivity, selectivity, response time, linearity, and dynamic range against various gas analytes such as dichloromethane, ethanol, natural gas, methane, formaldehyde and benzene) utilizing QCM. The highest sensitivity film immobilized with ionic liquids allowed the development of a ionic liquid composite-based sensor array to analyze complex mixtures utilizing structural differences and the extent of intermolecular interactions [28]. An electrochemical ethylene sensor was reported by employing a thin layer of ionic liquid as electrolyte. Ionic liquids served as an alternative electrolyte for many electrochemical gas sensors generally relied on a strongly acidic electrolyte. A detection limit of 760 ppb and a linear response up to 10 ppm were achieved in this work [29]. Next, an ionic liquid-mediated electrochemiluminescent sensor for the detection of sulfur dioxide has been developed. The portable system is based on the strong quenching effect of SO_2 on the electrochemiluminescent of the coreactant system in the ionic liquid film. This proposed SO_2 electrochemiluminescent sensor can be operated at room temperature and shows high selectivity, good reproducibility and long-term stability in a dry atmosphere [30]. A room temperature ionic liquid was used as a solvent for the detection of highly toxic methylamine and hydrogen chloride on Pt screen-printed electrodes. The achieved limit of detections were lower than the current Occupational Safety and Health Administration Permissible Exposure Limit, suggesting that Pt screen-printed electrodes can successfully be combined with ionic liquids as cheap alternatives for amperometric gas sensing [31]. Most recently, a gas sensing approach based on differential capacitance of electrified ionic liquid electrode interfaces in the presence and absence of adsorbed gas molecules was developed. The observed change of differential capacitance has a local maximum at a certain potential that is unique for each type of gas, and is concentration-dependent. Characterization of SO_2 detection was completed at ppb levels with less than 1.8% signal from other interfering species (i.e., CO_2, O_2, NO_2, NO, SO_2, H_2O, H_2 and cyclohexane, tested at the same concentration as SO_2) [32]. The aforementioned studies pave the way of utilizing ionic liquids for the development of gas sensing devices.

3.2. Reaction-based gas sensing ionic liquids on QCM

A new series of reaction-based SIL gas analysis system on QCM have been continuously developed in our laboratory. This SIL-on-QCM chip system not only is a cost-effective approach but also shows a great potential to detect a wide range of VOCs with high efficiency and specificity. In combination, the tunable chemical reactivity, negligible volatility, and good thermal stability of ionic liquids with high sensitivity of QCM sensor chips make this integrated platform highly attractive for chemoselective gas sensing. The negligible vapor pressure of ionic

liquids ensures that the sensors do not "dry out" on QCM chips and show free of leakage and the loss of loading during the measurement. As illustrated in **Figure 2**, when gases rapidly diffuse into the SIL thin film on QCM chips and specific chemical reactions for selective gases in ionic liquids occur under appropriate experimental conditions. The mass changes on QCM chips during the chemical reactions of a gas analyte and the tailored ionic liquid are readily obtained and ultimately transduced to generate an analytical signal. The thin coatings (200–300 nm thickness) of ionic liquids on the surface of the QCM chip (9 MHz) are achieved by depositing the diluted methanol containing SILs. The used SIL layer on QCM chip could be easily washed away by methanol and further replaced with a new SIL. This regeneratable SIL-on-QCM chip system can be performed at room temperature, and dried ambient air is used as carrier gas.

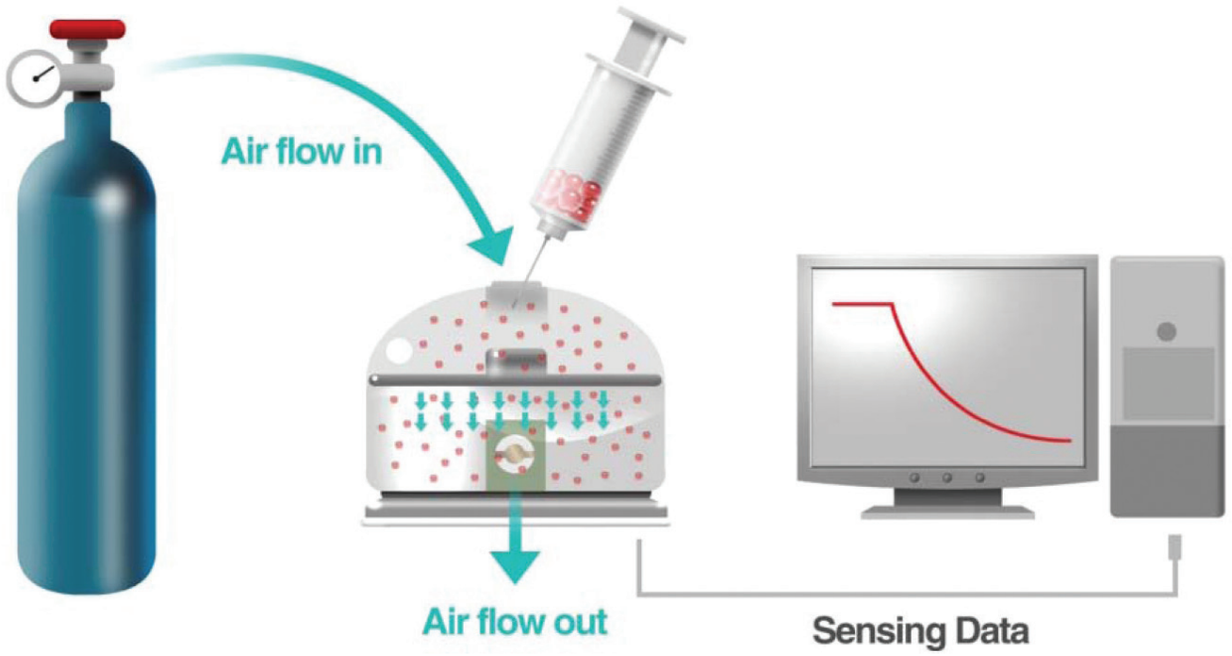

Figure 2. Schematic representation of a SIL-on-QCM gas analysis system for reaction-based gas sensing.

As shown in **Figure 3**, a series of chemoselective SILs for the detections of aldehyde, ketone, amine and azide gases have been prepared. This section is intended as a comprehensive update to our previous and recent works on the developments of SILs. **SIL 1** was first synthesized for the detection of aldehyde and ketone gases [33]. Interestingly, the results showed that **SIL 1** was more sensitive and selective to capturing aldehyde than ketone gases. To improve the sensitivity of ketone gas sensing, **SIL 2** was synthesized subsequently [34]. As the sensing reactions take place, **SIL 1** and **SIL 2** formed imine and hydrazone adducts with aldehydes and ketones, respectively (**Figure 4**). **SIL 1** displayed a similar reaction rate to aliphatic and aromatic aldehydes while **SIL 2** reacted efficiently with acyclic and cyclic ketone gases. It is noted that the irreversible nature of the frequency drops from QCM

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measurements of aldehyde and ketone sensing by both SILs suggesting a non-equilibrium formation of Schiff bases. Notably, this SIL-on-QCM chip system was totally insensitive to common VOCs such as methanol, ethanol, ethyl acetate, hexane and most importantly, moisture (water) ($\Delta F \sim 0$ Hz); that is, any water present in the gas stream would not be in any direct competition with target gases. The results of sensing aldehyde and ketone sensing prompted us to synthesize **SIL 3** for the detection of amine gases. The chemical reaction between **SIL 3** and amine gases was based on the transimination reaction. Although the model amine gas (propylamine) was detectable at low concentration (28.5 ppb), the minimal QCM response (~0.5 Hz) and seemly reversible in its signal were noticed. From a quick search of the literature, we realized that Lewis acids could notably facilitate the transimination reaction as well as imine and hydrazone forming reactions in conventional molecular solvents. We found that **SIL 3** with 1 mol% hint of $Sc(OTf)_3$ could catalyze the transimination reaction to produce the largest and irreversible QCM response ($\Delta F = 20$ Hz). The sensitivity of detection was also significantly improved about 11.4-fold for the model amine gas (28.5 ppb → 2.5 ppb). Remarkably, even the smallest molecular weight amine gas, ammonia, the detection limit could be achieved approximately 3.9 ppb ($\Delta F \sim 1.0$ Hz). With this in mind, we could expect to develop an ultrasensitive SIL for detection of ketone gases. Indeed, **SIL 2** with 2 mol% of $Sc(OTf)_3$ also could promote hydrazone formation and produce twofold increase and irreversible QCM response. With the addition of metal triflate, the detecting sensitivity of **SIL 2** was significantly down to 0.6 ppb for cyclohexanone and 1.1 ppb for acetone, respectively. Surprisingly, even the masked ketone gases such as 2,2-dimethoxypropane was also detectable at a level of 34 ppb.

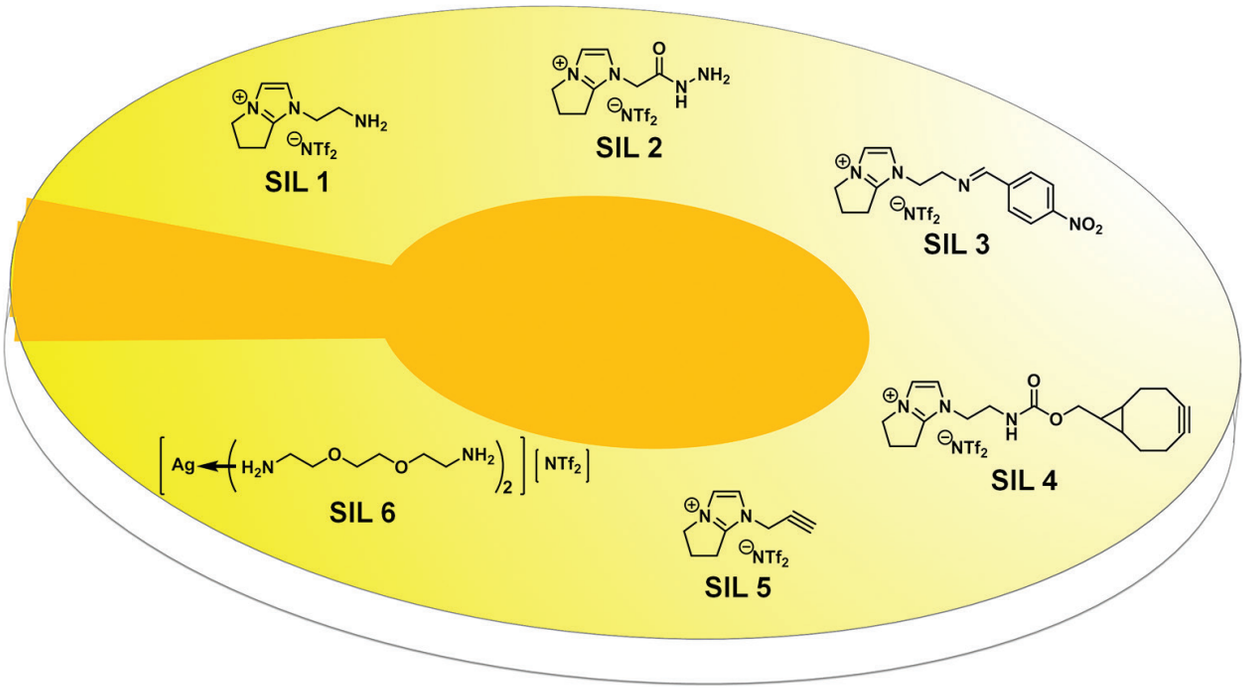

Figure 3. Chemical structures of SIL 1-6.

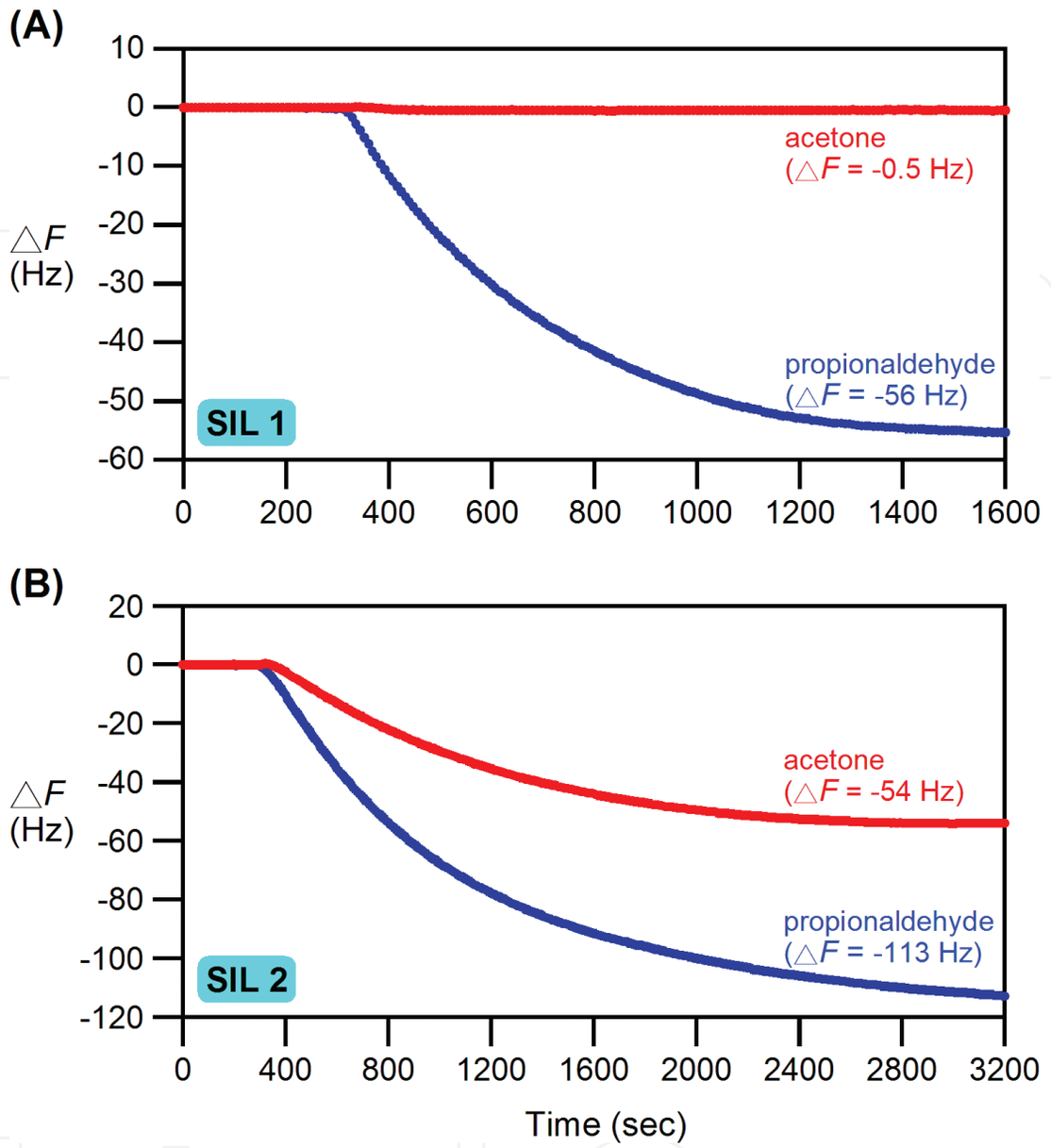

Figure 4. Chemoselective detection of acetone and propionaldehyde gases (98 ppb each) of identical molecular weight (C_3H_6O) by 9 MHz QCM thin coated with (A) **SIL 1** and (B) **SIL 2** (3.3 nL each, 300 nm thickness). Air was used as the carrier gas with a flow rate of 3 mL/min, and gas samples were injected at 300 s. The resonance frequency drop (ΔF) is the QCM response on the quartz chip surface.

Next, on the basis of the recent advances in click chemistry, the Huisgen 1, 3-dipolar azide and alkyne [3+2] cycloaddition, we synthesized **SIL 4** and **5** for the chemoselective detection of organic azide gases [35]. Compared to the unstrained **SIL 5**, we can expect that the strained **SIL 4** should possess much greater enhancement in reactivity toward organic azides. Indeed, **SIL 4** showed high sensitivities toward both aliphatic and aryl azide gases, but **SIL 5** was totally inert toward azide gas sensing (**Figure 5**). Among all azide gases investigated, the sensitivity of detection was 5 ppb for benzyl azide and 35 ppb for butyl azide, respectively. It is noted that the reactivity order of benzyl azides > phenyl azides > allyl azides toward **SIL 4** could be understood by the reported activation energy [36]. In addition, **SIL 4**

could be applied to detect azide gases with dual functional groups such as 2-azioethyl amine. Most remarkably, **SIL 4**, which carries a reactive alkyne dienophile group, can also readily capture cyclopentadiene gas at low ppb (65.5 ppb) through the Diels-Alder [4+2] cycloaddition reaction [35]. Namely, **SIL 4-**based upon cycloaddition reactions is well-suited to detect both azide and diene gases with a high sensitivity.

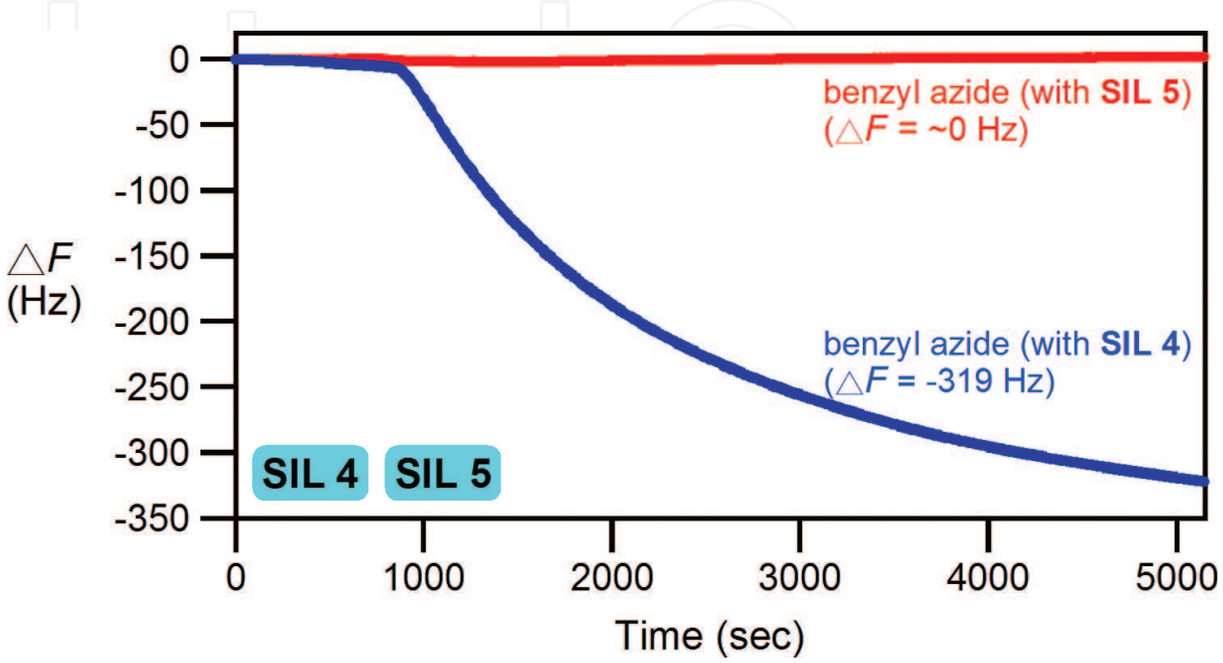

Figure 5. Chemoselective detection of benzyl azide gas (146 ppb) by 9 MHz QCM thin coated with **SIL 4** and **SIL 5** (3.3 nL each, 300 nm thickness). Nitrogen was used as the carrier gas with a flow rate of 3 ml/min, and gas samples were injected at 1000 s. The resonance frequency drop (ΔF) is the QCM response on the quartz chip surface.

Recently, transition metal-containing ionic liquids have received significant research attention. Due to the strong affinities between transition metal ions and neutral alkylamines, transition metal-containing ionic liquids can be easily prepared under convenient reaction conditions (e.g., aqueous solution and room temperature) with high efficiency. Furthermore, there is no tedious organic synthesis steps involved but only simply sample mixing followed by straightforward extraction workups. Thus, we synthesized a new transition metal-containing ionic liquids, **SIL 6**, for detecting exclusive for aldehyde gases from an inexpensive and commercially available alkylamine, 1, 2-bis(2-aminoethoxy)ethane as the ligand for silver (I) [37]. Unlike the synthesis of imidazolium-based **SIL 1** that required four synthetic steps with a low yield (37%), the preparation of **SIL 6** could be achieved by only straightforward mixing of silver and amine reagents with a moderate high yield (66%). **SIL 6** was totally insensitive to the ketone gases. Notably, with the same concentration of model aldehyde gas (propionaldehyde, 100 ppb), **SIL 6** displayed a stronger QCM response (ΔF = -40 Hz) than **SIL 1** (ΔF = -19 Hz) (**Figure 6**). Despite silver ionic liquids having the apparent but inherent drawback that they are less stable toward light, they process many advantages such as only minute amounts of SILs (10–15 nL per quartz chip) are consumed. In addition, no chemical immobilization on quartz chips is needed, plus they can be readily regenerated by simply

washing them away. Finally, the SIL platform developed in this work is highly chemoselective (**SIL 1** and **SIL 6**: specific to aldehyde, **SIL 2**: sensitive to ketone, **SIL 3**: specific to amine, and **SIL 4**: selective to azide gases, respectively) with superior gas reactivity for **SIL 6** than the imidazolium-based **SIL 1** and, most significantly, totally insensitive to moisture.

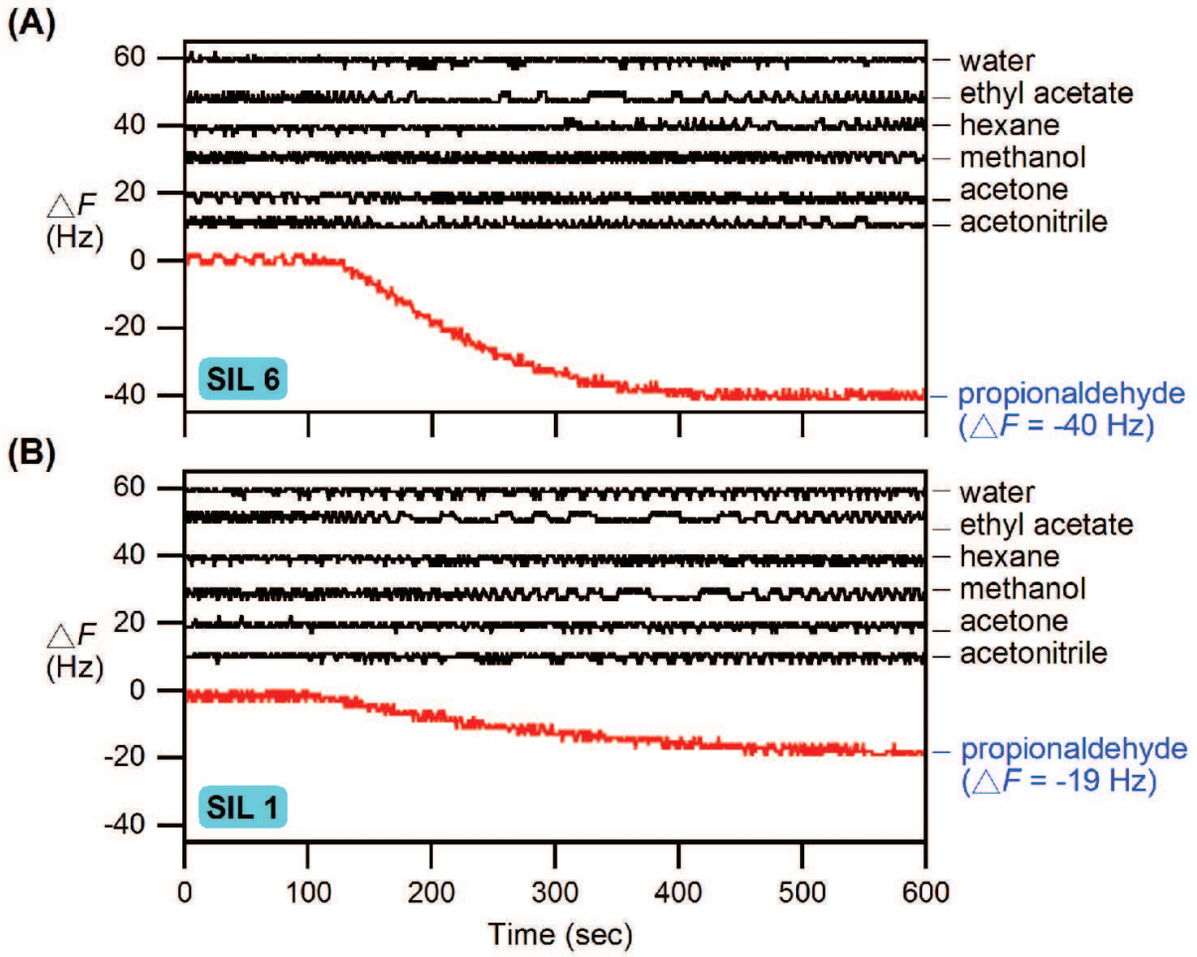

Figure 6. Chemoselective detection of water, ethyl acetate, hexane, methanol, acetone, acetonitrile and propionaldehyde gases (100 ppb each) all by a multichannel QCM thin coated with (A) **SIL 6** and (B) **SIL 1** (33 nmol each, 200–300 nm thickness). The QCM sensograms for water, ethyl acetate, hexane, methanol, acetone and acetonitrile gases were vertically shifted (10 Hz in between) for clarity. Nitrogen was used as the carrier gas with a flow rate of 3 mL/min, and gaseous samples were injected at 100 s. The resonance frequency drop (ΔF, in Hz) is the QCM response on the quartz chip surface.

4. Conclusion

Ionic liquids are commonly defined as molten organic salts, which have been used in analytical sciences and biosensing technologies by harnessing the transformation in chemical structure and hence fine-tuning their physiochemical properties. A myriad of assays can be performed in ionic liquids and a plethora of composite materials based on carbon nanotubes, graphene, graphite, metal nanomaterials, polymers and sol–gels have demonstrated their usefulness in biosensors. However, there are few examples of gas sensors exploiting

the properties of ionic liquid. Gas sensing systems based on different principles have been developed for real-time detection of human-made or naturally occurring VOCs including QCM. In light of the potential problems of many gas sensors, the electromechanical device, QCM represents an excellent platform if sensitive, selective and versatile sensing materials were available. To this end, we have developed a series of ultrasensitive SILs that are capable of detecting VOCs selectively. SILs on QCM detect VOCs by sensing normally neglect changes in weight on a nanogram level. Target analytes are captured by SILs and the accumulated weights are transduced into frequency shifts on QCM. An integrated multichannel system could be crafted to efficiently detect and optimally exploit the advantages of various SILs for various VOCs sensing simultaneously. We thus anticipate the design of a pattern recognition library of chemical sensor arrays in the future. Finally, the ultimate goal would be SILs on QCM electronic nose system to "smell" as good as mammalian olfaction or better.

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Author details

Yi-Pin Chang[1] and Yen-Ho Chu[2]*

*Address all correspondence to: cheyhc@ccu.edu.tw

1 The Forsyth Institute, Cambridge, MA, USA

2 Department of Chemistry and Biochemistry, National Chung Cheng University, Minhsiung, Chiayi, Taiwan, ROC

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