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Exploring Silver Ionic Liquids for Reaction-Based Gas Sensing on Quartz Crystal Microbalance†

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Reaction-based, sensitive sensing of aldehyde and ketone gases in real time was effectively achieved on QCM chips thin-coated with silver ionic liquids SIL 1 and SIL 4, respectively. The method platform developed in this work involves straightforward synthesis of functional silver ionic liquids in water, and is label-free and highly chemoselective with superior gas reactivity for SIL 1 and SIL 4 and, most significantly, totally insensitive to moisture.

Transition metal-containing ionic liquids, in addition to the common organic ionic liquids, have recently gained notable research attention. These metal ionic liquids possess advantages such as their high solubility of metal salts and strong response to magnetic field that much outperform common organic ionic liquids. Furthermore, metal ionic liquids are attractive electrolytes of very high metal concentration for efficient electrodereposition. Recently, Binnemans and Fransaer, Huang and Dai and their co-workers have demonstrated that silver ionic liquids, for example, are superior electrolytes for electrodereposition of metallic silver with high current density. Moreover, due to the nature of their weaker interactions between the cations and anions in metal ionic liquids than those in organic ionic liquids, silver ionic liquids typically are of low viscosity. We therefore envisioned that metal ionic liquids in principle should carry unique mass transport property and thus these novel materials may prove valuable for new chemistry applications. In this work, we report a new use of silver ionic liquids SIL 1, 2 and 4 (Fig. 1) for the reaction-based sensing measurement of volatile organic compounds (VOCs) on quartz crystal microbalance (QCM).†

Transition metal ions are known for their strong affinities with neutral alkylamines. Silver ionic liquids [Ag(L)2][NTf2] are composed of a cation with the silver ion self-assembled by two alkylamine ligands (L) and a [NTf2] anion. For these silver complexes,

(Fig. 1) Structures of silver ionic liquids SIL 1, 2 and 4. Also included is the structure of an amine-functionalized, imidazolium-based sensing ionic liquid SIL 3 previously synthesized and studied in our laboratory.

two alkylamine ligands have been demonstrated to associate in a linear geometry with the silver cation. When compared with organic ionic liquids, the synthesis of metal ionic liquids is green as they could be readily prepared in water, involves no tedious organic synthesis steps but only sample mixing followed by straightforward extraction workups and, most significantly, can often be carried out at convenient temperatures. In this work, we selected commercially inexpensive 1,2-bis(2-aminoethoxy)ethane (for SIL 1) and 2-methoxethylamine (for SIL 2), and synthetically obtainable 1,2-bis(2-aminoethoxy)ethane (for SIL 4; 51% isolated yield in 2 steps, see Fig. S1 in ESI‡ for its detailed preparation) as ligands for silver (I), so that the resulting silver ionic liquids (Fig. 1) could be used directly to give chemoselective measurements to VOCs such as aldehydes and ketones at ambient temperature. The hydrophobic [NTf2] anion was selected in this study primarily because of the known low viscosity in their final forms and chemically inertness to moisture. Here, SIL 2 was used as the control ionic liquid.

The protocol developed by Huang and co-workers§ was modified to synthesize all silver ionic liquids studied in this work. For the preparation of control ionic liquid SIL 2, silver nitrate in water was first treated with 2-methoxethylamine in a 1:2 metal-to-ligand mole ratio with minimum light exposure during synthesis. This

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‡Electronic Supplementary Information (ESI) available: Fig. S1-S5; experimental procedures, H & 13C NMR and ESI-HRMS spectra and data of SIL 1, 2 and 4; QCM measurements (24 pages). See DOI: 10.1039/A0xx00000x
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aqueous solution containing Ag\(\text{L}_2\)\(^{+}\) was then mixed homogeneously with LiNTf\(_2\) in water for salt metathesis (1:1 mole ratio). The solution mixture became two phases usually within 30 min in which the desired hydrophobic ionic liquid \(\text{[Ag(L)]}[\text{NTf}_2]\) was in the bottom phase. Lastly, this ionic liquid SIL 2 was extracted using dichloromethane and could then be conveniently purified by washing with deionized water twice to ensure the complete removal of LiNO\(_3\) and, if any, residual AgNO\(_3\) and amine. Other functional silver ionic liquids SIL 1 and 4 were prepared in similar manners but using a syringe pump to purposely deliver slowly (2 h) an aqueous AgNO\(_3\) solution into the solution containing 1,2-bis(2-aminoethoxy)ethane or 1,2-bis(2-aminooxyethoxy)ethane ligand in water. The mole ratio of silver to the ligand was 1:1.98 to avoid the potential formation of \(\text{[Ag(L)]}_m\) oligomers or polymers but ensure the synthesis of the desired \(\text{[Ag(L)]}[\text{NTf}_2]\) ionic liquids SIL 1 and 4 (ESI†). The isolated yields of all SIL 1, 2 and 4 syntheses were high: 66, 94 and 78%, respectively. All silver ionic liquids prepared in this work are liquid at room temperature. Details such as synthetic procedures, \(^1\)H, \(^13\)C NMR and ESI-HRMS spectra and data of SIL 1, 2 and 4 are summarized in the ESI†. The SIL 3 was previously synthesized and reported by us.\(^{35}\)

Our gas sensing experiments were performed on a prototypic multi-channel, low (1 Hz) resolution QCM device.\(^{30}\) Results shown in Fig. 2A demonstrate that, using the same concentration (100 ppb) for all gases tested, the SIL 1 reacted selectively only with propionaldehyde (\(\Delta F = -40\) Hz). This reaction-based, SIL-on-chip prototype system worked well and was totally unreactive and insensitive to common VOCs such as ammonia, chloroform, dichloromethane, ethyl acetate, hexane, methanol, acetonitrile and, most significantly, moisture (\(\Delta F = 0\) Hz), indicating that any residual water present in the gas stream would not interfere and be in direct competition with the aldehyde (Fig. 2A). In our hand, SIL 1 was insensitive to the less reactive ketone functional group in acetone gas at 100 ppb (Fig. 2A). Also, its irreversible frequency drop of propionaldehyde with the hydrophobic SIL 1 suggested the nonequilibrium formation of an imine product,\(^{36}\) confirming its excellent reactivity: reaction time \(\sim 300\) s (Fig. 2A). \(^1\)H NMR analysis (in CDCl\(_3\)) further supported the Schiff base formed from SIL 1 reaction with propionaldehyde: a characteristic aliphatic imine CH=N signal at 7.84 ppm was experimentally obtained. Furthermore, this SIL 1 unambiguously outperformed the control SIL 2 (\(\Delta F = 0\) Hz, Fig. 2B) and the imidazolium SIL 3 (\(\Delta F = -19\) Hz, Fig. 2C), proving that SIL 2 containing a monoamine as the ligand was totally inert to propionaldehyde as well as all other gases tested during the entire reaction time and, as a result, the irreversible frequency drop in this continuous flow QCM measurement was not due to any nonspecific dissolution of aldehyde gas in ionic liquids (Fig. 2A-2C). The smallest aldehyde, formaldehyde, also reacted well with SIL 1, but not the control silver ionic liquid SIL 2, and was readily detected by QCM (\(\Delta F = -19\) and 0 Hz, respectively; Fig. S2, ESI†). In the case of ammonia gas reaction with the SIL 2 thionated on the quartz chip (top sensorgram in Fig. 2B), we found that, albeit detectable at 100 ppb, the QCM response was minimal and reversible in its signal, likely due to its nonspecific dissolution of ammonia gas in SIL 2 ionic liquid. Unlike the synthesis of SIL 3 that demanded multiple synthetic steps,\(^{36}\) the preparation of SIL 1 required only straightforward mixing of silver and amine reagents.

Fig. 3A provides much detailed quantitative studies of SIL 1 reactions with propionaldehyde and acetone gases of identical molecular weight (C\(_3\)H\(_6\)O). Both gases showed linear QCM frequency responses within the range of concentrations (60-1050 ppb) investigated (Fig. S3B). This SIL 1 is highly selective to aldehyde gas: at 2 Hz drop (\(\Delta F\)) in resonance frequency, the sensitivity of detection was 4.6 ppb for propionaldehyde and 139 ppb for acetone, respectively; that is, an approximately 30-fold higher sensitivity in detection for aldehyde than that of ketone gas of the same mass was observed.

Our promising results of propionaldehyde gas sensing by SIL 1 (1–2 and 3) prompted us to further investigate its general applicability
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Fig. 5 Chemoselective detection of acyclic and cyclic ketone gases (200 ppb each) all by QCM thin-coated with SIL 1, SIL 2, and SIL 4 (33 n mole each). The sensorgrams from SIL 1 and SIL 2 were vertically shifted (25 Hz and 50 Hz, respectively) 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.

cyclohexanone (ΔF = -113 Hz). For other three ketones examined, SIL 4 is significantly less reactive toward 2-cyclohexen-1-one (ΔF = -20 Hz) > cyclopentanone (ΔF = -13 Hz) ≈ aromatic acetonophenone (ΔF = -12 Hz) (Fig. 5). Both SIL 1 and SIL 2 were totally inert to all ketone gases tested. All these preliminary results confirmed that SIL 4 is chemoselective and sensitive toward capturing ketone gases.

Many gases such as manmade or naturally occurring VOCs can adversely affect human health or cause harm to the environment. Despite protocols being available for their detection, new sensing technologies are nevertheless of considerable importance, especially when their direct access from readily available reagents could be secured under mild conditions. In this work, we have successfully synthesized functional silver ionic liquids for online and label-free sensing of volatile aldehyde and ketone compounds in real time. These silver ionic liquids were conveniently prepared in water. Our reaction-based gas sensing approach consumes only minute amounts of SILs (10-15 mL per quartz chip), does not require any chemical immobilization on quartz chips, and can be readily regenerated by washing away the used SILs and replacing the new ones. The SIL platform developed in this work is highly chemoselective (SIL 1, specific to aldehyde and SIL 4, sensitive to ketone gases, respectively) with superior gas reactivity for SIL 1 than the imidazolidine-based SIL 3 (Fig. 2) and, most significantly, totally insensitive to moisture. An apparent but inherent pitfall of silver ionic liquids is that they are less stable towards light. In addition, since SIL 1 and SIL 4 amine ionic liquids were prepared in water, they most likely were partially protonated and therefore found insensitive toward acid gas (Fig. S5, ESI†). Our work presented here nevertheless sets the stage for continued expansion of the applications for silver ionic liquids. To our knowledge, this is the first report demonstrating fast and sensitive aldehyde and ketone gas sensing with silver ionic liquids on QCM. We envision developing a collection of functional metal ionic liquids tailored for use as gas sensing ionic liquids. These metal ionic liquids will bolster efforts to detect complex VOCs in working environments and for disease diagnosis.

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Notes and references

10. A 9 MHz QCM prototype device used in this work was composed of an outer metal chassis of ADS (affinity detection system) (ANT Technology Co., Taipei, Taiwan; http://www.anttech.com.tw/) and a QCM S801B Analyzer core unit (Smart Biotechnology, Taipei, Taiwan).
11. Both SIL 1 and SIL 4 capture aldehyde gases (for the smallest formaldehyde gas detection, see Fig. S2 in ESI†: ΔF = -19 and -93 Hz, respectively), but only SIL 4 selectively and effectively reacts with ketone gases in low ppb concentration.
15. The final SILs were prone to decomposition by light. If not, additional care was taken to exclude light, then the SILs slowly turned into one of the following results: a dark coloration,
settling out of a black fine powder of colloidal silver or a shiny metallic silver coating on the storage vessel. These SILs were therefore necessary stored in the dark and found stable for three months, at least, in freezer temperatures.