

VOC Sensing in Humid and Dry Environments

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Abstract - We report the development of gas-sensing multicomponent hybrid materials to be used under humidified and dried environments without the need of sample preconditioning or heavy signal processing. The easy tunability and the unique characteristics presented by the multicomponent hybrid suggests their use in near-term applications in electronic nose systems able to operate in dry or humidified environments.

Keywords - hybrid gel, ionic liquid, liquid crystal, humidity, gas sensing

I. INTRODUCTION

Humidity is everywhere on earth. One of the most challenging goals in gas sensing and artificial olfaction is the detection and measurement of volatile organic compounds (VOCs) in environmental conditions where humidity is present. Most common gas sensors, such as metal oxide conductors or conducting polymers, are influenced by the presence of humidity leading to variations in their signals due to cross reactivity. To avoid signal interference, electronic nose systems typically incorporate additional features such as use of nitrogen or dry air as a sample carrier, the use of sample preconditioning chambers or coating the sensing material with hydrophobic layers [1]–[3]. The possibility to tune the effect of humidity in gas sensing materials is very appealing. Multicomponent materials are promising alternatives to build gas sensing arrays due to the possibility of combining different component sensing properties within a single material. Gas-sensing multicomponent hybrid gels are gel-like stable biopolymeric matrices with embedded ionic liquid-liquid crystal droplets [4], [5]. The unique conjugation results in chemically versatile materials possessing ionic conductivity, due to the presence of ionic liquids, and optical properties, due to the presence of ionic liquid-liquid crystal droplets. Upon interaction with VOCs or gases, these properties change due to the droplets reconfiguration and/or differences in the conductance of the biopolymeric matrix [4], [5]. Moreover, ionic liquids are considered “design solvents” as they are molten salts completely composed by cations and anions, allowing an infinity of combinations with different physico-chemical properties.

In this work, we focused on the variation of the ionic liquid component by rationalizing the combination of the

anion and the cation towards the development of multicomponent hybrid gels with different hydrophilicity character.

II. VOC-SENSITIVE HYBRID MATERIALS

In 1-butyl-3-methylimidazolium-based ionic liquids, [BMIM][X], the counterion [X]⁻ plays a dominant role in the interaction of the ionic liquid with water [6], [7]. In this sense, multicomponent hybrid materials containing gelatin, the liquid crystal 4-Cyano-4'-pentylbiphenyl (5CB) and the ionic liquid with [BMIM]⁺ cation combined with different anions were produced. The counterions chosen were dicyanamide [DCA]⁻ and chloride, [Cl]⁻, due to their different hydrophilicity and hydrogen acceptor properties. In particular, the use of the ionic liquid [BMIM][DCA] in the hybrid material formulation gave rise to a self-supporting gel, where no flow was observed upon the vial inversion test. On the contrary, for [BMIM][Cl]-based hybrid material, flow was observed suggesting a viscous solution (Fig. 1). These differences might be mainly related with ionic liquid anion differences regarding its volume, hydrogen bond ability and affinity towards water molecules. The [Cl]⁻ anion is hydrophilic, establishing strong hydrogen bonds with water. In fact, and according to the empirical Kamlet-Taff parameters, when associated with [BMIM]⁺ cation, the anion [Cl]⁻ presents a higher hydrogen bond acceptor ability (β) than [DCA]⁻ anion (0.95 and 0.64, respectively) [8]. Therefore, [Cl]⁻ anion will form hydrogen bonds with water stilling the amount of molecules need to allow the crosslinking between gelatin polypeptide chains.

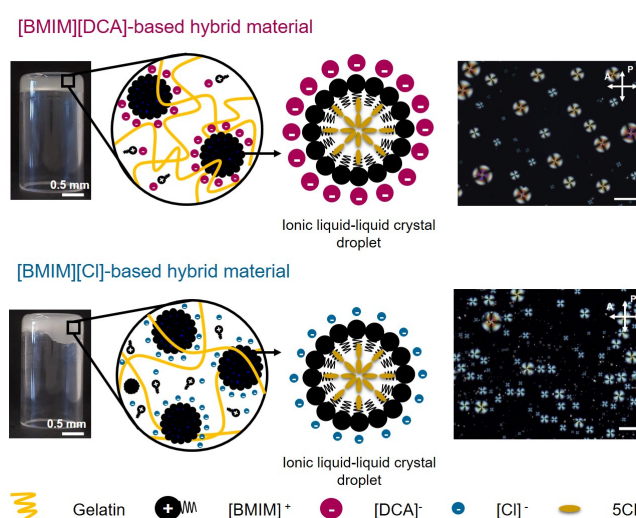


Fig. 1. [BMIM][DCA] and [BMIM][Cl] gelatin hybrid materials: macroscopic images, schematic representation and polarized optical microscopy images.

For both [BMIM][DCA] and [BMIM][Cl]-based hybrid materials, it was observed that the liquid crystal molecules

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adopt a radial configuration, exhibiting the typical Maltese cross observable under Polarizing Optical Microscopy with crossed polarizers (Fig. 1). Upon exposure to VOCs the molecular ordering of the liquid crystal molecules changes from radial to isotropic. This process is reversible upon VOCs desorption from the gel surface and is the basis for optical sensing.

III. VOC SENSING DEVICE

The studies were performed in an in-house tailor-made VOC sensing device (Fig. 2a). The different VOC (ethanol, acetone, toluene and hexane) concentrations in dry or humid environments were generated through changes in the flow rates of the mass flow controllers (MFC, Fig. 2a). During VOC exposure periods, the nitrogen gas, feeding the MFC 2, was bubbled in the pure solvent to generate VOC vapor. MFC 1, also fed with nitrogen gas, was directly mixed with the VOC vapor at the inlet of the detection chamber in the case of a dry environment (0% RH) or first bubbled through NaBr to generate a humid environment (50% RH). During the recovery periods only the MFC 1 stream entered the detection chamber. To generate the different VOC concentrations, MFC 1 was set at a fixed flow rate (1.5 slpm, for ethanol, toluene and hexane or 5.0 slpm, for acetone) while MFC 2 was programmed to slowly change (increments of 0.05 slpm) the flow rate for the interval 0.05-1.5 slpm. Each step comprised of 5 exposure/recovery cycles generated by a two-way solenoid valve programmed to alternately direct the nitrogen carrier stream to the exposure or the recovery path using an automated temporized switching. During the exposure period the valve was on for 5 seconds while in the recovery period, it was off during 15 seconds. A custom made python script (Python 3.7, using alicat library 0.2.2) was used to program the carrier MFC and solenoid valve operation, an to synchronize them with the detection chamber and the humidity sensor [9].

The [BMIM][DCA]- and [BMIM][Cl]-based optical sensors (Fig. 2b) were placed simultaneously in the detection chamber of the VOC-sensing device between crossed polarizers. During the exposure/recovery cycles, the sensors were illuminated by a LED and the light changes were measured using a photodiode [5].

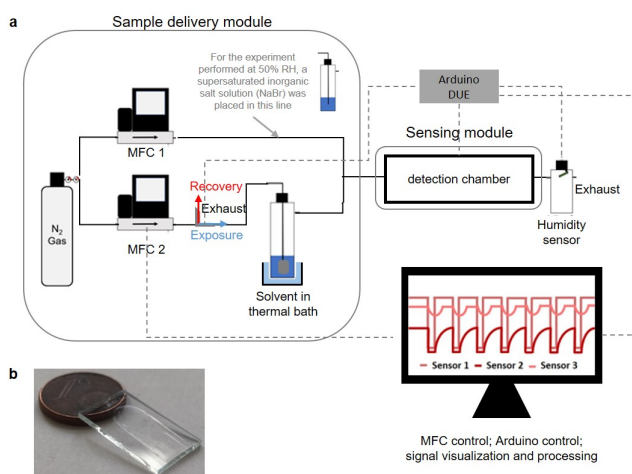


Fig. 2. (a) In-house tailor-made VOC-sensing device: schematic representation. (b) Macroscopic image of an optical sensor.

IV. VOC SENSING USING HYBRID MATERIALS IN HUMID AND DRY CONDITIONS

[BMIM][DCA] and [BMIM][Cl]-based hybrid sensors capability of VOC sensing under dried (0% RH) and humidified (50% RH) conditions was evaluated by exposing them sequentially to 29 concentrations of four model VOCs with different polarity and hydrophilicity [4], [10]: ethanol, acetone, toluene and hexane. Sensor changes were monitored during 5 cycles of exposure to each of the VOC concentrations, followed by exposure to a N₂ stream for the recovery of the sensors. Before VOC exposure, a 15 minutes' equilibration period was applied to the sensing materials. In addition, it was also performed a blank assay using the same conditions (humidity and nitrogen flow) as the ones from the experiments in order to identify possible signals contaminations. While [BMIM][Cl]-based hybrid materials did not respond to small RH variations of the nitrogen stream, [BMIM][DCA]-based hybrid materials did, being observed small signal variations (data not shown). However, the relative amplitude of these were not significant when compared to the ones observed upon exposure to VOCs.

In general, lower amplitude signals were obtained during VOC exposure to 0% RH when comparing with 50% RH (Fig. 3). In fact, at 0% RH, [BMIM][DCA]-based hybrid materials showed no response when exposed to the VOC. When submitted to low humidity (under 20% RH) environments, the liquid crystal 5CB is isotropic and therefore the optical probes are not functional [9].

Ethanol is a polar protic solvent and hydrogen donor, with favorable adsorption in ionic liquids [8]. Therefore, ethanol molecules will tend to have higher interaction with gelatin and water molecules or with the ionic liquid anion. In this case, interactions with liquid crystal molecules are less likely to occur due to its hydrophobic character. When the hybrid materials are exposed to ethanol, is more likely that the optical response is associated with changes in the matrix combined with small disturbances on the liquid crystal order as ethanol molecules might interact with ionic liquid anion present at the surface of the droplets. At 50% RH, both [BMIM][DCA] and [BMIM][Cl]-based hybrid materials presented a detection limit of 1% (v/v) and a saturation concentration at 3.3% (v/v). At 0% RH, [BMIM][Cl]-based hybrid material did not present a quantitative response. Acetone, toluene and hexane possess different polarity characters. Nonetheless, a similar behavior is observed in optical response of the hybrid materials when exposed to these VOCs which is related with the "domino effect". In these cases, it is required to achieve a minimum concentration of VOC molecules at the surface of the hybrid material to trigger the perturbation of liquid crystal molecules and further change to isotropic configuration. VOC concentration below that concentration generate minimal responses, while above it the optical response is saturated (Fig. 3). The lowest detection limit (0.53% (v/v)) was observed for toluene which also presented the lowest saturation concentration (1.4-1.8% (v/v)). On the contrary, the high detection limit was obtained when the hybrid materials are exposed to hexane (7-8% (v/v)). Acetone is a polar aprotic solvent and a hydrogen bond acceptor. As such, acetone molecules might interact with the interface of the ionic liquid-liquid crystal droplets, through hydrogen bond with acidic hydrogen of the ionic liquid cation imidazolium

ring [BMIM]⁺ and through cation-dipole electrostatic interactions. Toluene is an aromatic compound that can performed π - π interactions also at the interface of the ionic liquid-liquid crystal droplets with imidazolium ring headgroup of the cation [BMIM]⁺. Finally, hexane molecules are likely to enter the droplet in order to preferentially interact with the ionic liquid cation alkyl chain or liquid crystal molecules, 5CB.

Comparing with other liquid crystal-based VOC sensing systems [11], our sensing device is faster, showing response times within 3-5 seconds.

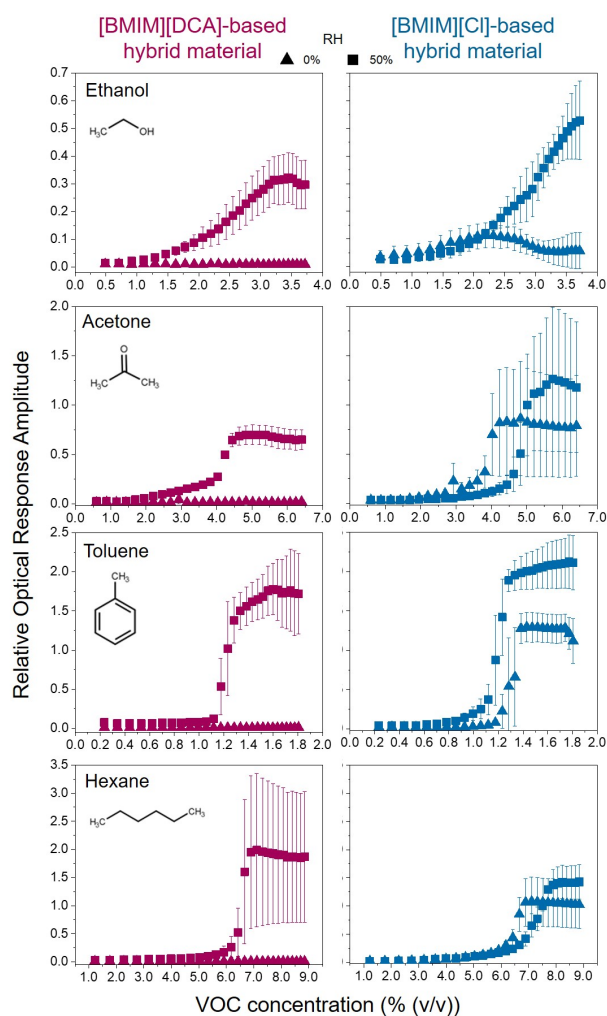


Fig. 3. [BMIM][DCA] and [BMIM][Cl] hybrid material thin films relative optical response amplitude when exposed to ethanol, acetone, toluene and hexane vapours at different concentrations under dried (\blacktriangle , 0% RH) or humidified (\blacksquare , 50% RH) conditions. ($n > 10$).

V. CONCLUSIONS

This work represents an example of the potential and versatility of multicomponent hybrid gels. A simple change of the ionic liquid anion in the formulation of the biobased

materials is directly reflected on the performance of the multicomponent hybrid gels as VOC sensing materials in dried and humidified environments. The hybrid material comprising a more hydrophilic ionic liquid anion in its composition ([Cl]⁻) allows the detection of the four tested VOCs (ethanol, acetone, toluene and hexane) at 0% and 50% RH, while the one with the less hydrophilic ionic liquid anion ([DCA]⁻) only allows VOC detection at 50% RH. Furthermore, VOC sensing response time are lower when compared with other liquid crystal-based systems [11].

The composition of multicomponent hybrid gels can be further tuned to lower VOC detection thresholds and optimize selectivity. Strategies such as adding VOC targeting moieties, playing with the structure of the ionic liquids or liquid crystals provide the possibility to rationalize and design tailor-made gas sensing materials that can be used under dried and humidified conditions, with potential application in gas sensing and artificial olfaction.

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