ENHANCED GAS SENSING WITH SOFT FUNCTIONAL MATERIALS

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ABSTRACT

The materials described in this work result from the self-assembly of liquid crystals and ionic liquids into droplets, stabilized within a biopolymeric matrix. These systems are extremely versatile gels, in terms of composition, and offer potential for fine tuning of both structure and function, as each individual component can be varied. Here, the characterization and application of these gels as sensing thin films in gas sensor devices is presented. The unique supramolecular structure of the gels is explored for molecular recognition of volatile organic compounds (VOCs) by employing gels with distinct formulations to yield combinatorial optical and electrical responses used in the distinction and identification of VOCs.

Index Terms — gel, liquid crystal, biopolymer, ionic liquid

1. INTRODUCTION

Supramolecular assembly is an attractive approach to rationally design functional biomaterials with the desired properties. It has been used to tune physicochemical and mechanical properties [1], but the concept of cooperative assembly of different molecules is also promising to engineer molecular recognition. In olfaction, molecular recognition processes are the first step on the identification of odours. Namely, an important challenge of artificial noses is the lack of selectivity of the sensors. Supramolecular assemblies represent a new approach to tune selectivity.

Liquid Crystals (LC), ionic liquids (IL) and biopolymers (BP) possess self-assembling properties [2]–[5] and have been explored in gas sensing [6]–[8]. However, their potential for cooperative self-assembly in a single material combining the properties of IL, LC and BP has not been exploited so far.

This work presents a new class of VOC-sensitive materials formed by the cooperative supramolecular assembly of IL and LC in droplets which are supported in a BP matrix (Fig. 1a) [9]. Transparent, self-supporting and flexible gels are obtained, which can be cast as films over untreated glass slides (Fig 1b). Each component has a function in the assembly of the material and in gas sensing. Distinct physicochemical properties are achievable by varying each of the individual components of the formulation, potentiating diversity and tuning VOC selectivity.

2. VOC-SENSITIVE GELS

Due to the dynamic balance of hydrophilic and hydrophobic intermolecular interactions, LC molecules are confined inside the LC-IL droplets, surrounded by a matrix of gelatin (Fig. 1a) [9]. The IL promotes the anchoring of LC normal to the droplets' interface and also participates in the dissolution of the biopolymer through ionic, electrostatic and hydrogen bonding with the polymer chains.

The supramolecular structure is intimately related with the gels' gas-sensing function as it allows the coexistence of optical and electrical responses in the same sensor, a unique property of these gels.

Due to the induced anchoring, LC molecules adopt a radial configuration, exhibiting typical optical textures observable under Polarizing Optical Microscopy (POM) with crossed polarizers (Fig. 1c). Upon exposure to VOCs, the molecular ordering of the LC changes from radial to isotropic, a process that is reversible when VOCs are desorbed from the gels. This phenomenon is the basis for optical VOC sensing.

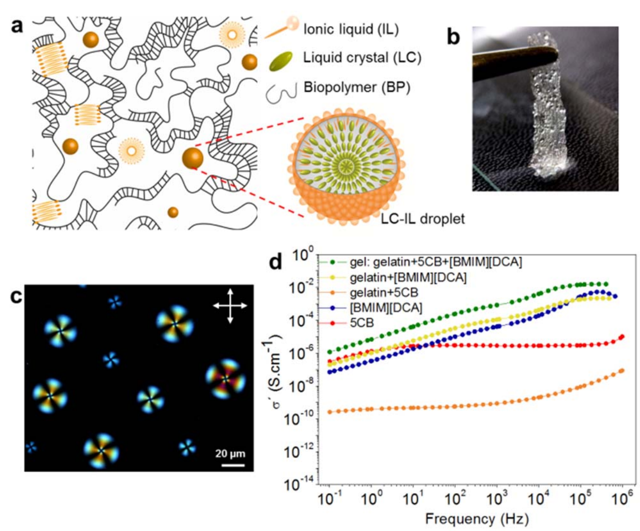

Fig. 1. Gels composed by the biopolymer gelatin, the ionic liquid [BMIM][DCA], the liquid crystal 5CB and water. (a) Schematic representation of the supramolecular organization within the gels. (b) Macroscopic appearance of a gel film. (c) POM image of a gel film, taken with crossed polarizers. (d) Real part of the conductivity spectra of the gel, control samples and neat constituents.

Furthermore, when polymers are dissolved in IL, conductive gels, known as ionogels [4], are obtained. Gelatin,

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in particular, has been shown to form versatile conductive materials [8]. By adding LC to this formulation, the gel acquires optical properties and an enhanced conductivity (Fig. 1d). When VOCs adsorb to the gel, there is an increase in the motility of IL's ions and therefore, the gel's admittance increases [10], a reversible process upon VOC desorption. This is the basis for electrical VOC sensing.

Overall, the gels combine the gas-sensing potential of liquid crystals and ionogels, and respond fast, within 5 s of exposure to VOCs, about 1/3 of the time reported in other works [11].

3. VOC-SENSING DEVICE

Prototype VOC-sensing devices were assembled in-house using low cost hardware options and the open access programming language Python (Fig. 2). The optical and opto-electrical versions of the device have a common structure (Fig. 2a), a similar detection chamber (Fig. 2b) and employ ambient air as sample carrier and recovery gas [12].

For optical sensing, each element of the sensor array (Fig. 2c) is comprised by a gel glass slide placed between crossed polarizers. The gel is illuminated by a LED and the light intensity exiting the gel is measured by a photodiode, enabling gas detection.

For electrical sensing, the gel is spread over interdigitated electrodes deposited on the glass slide (Fig. 2c). Electrical gas sensing is based on the measurement of the gel conductivity upon VOC adsorption and desorption.

For opto-electrical sensing, the sensing module includes both transducing systems and the gel slide combines both optical and electrical sensing areas (Fig. 2c). Optical and electrical signals are then obtained by alternately exposing the sensors to the gas sample and to air.

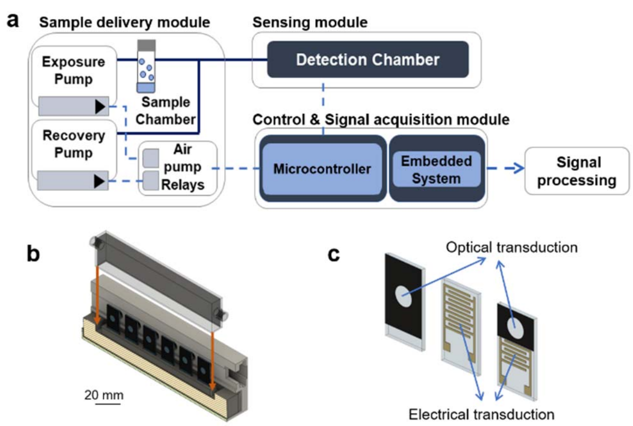

Fig. 2. Custom-made gas sensing device. (a) Schematic representation, where the microcontroller is Arduino Due and the embedded system is Raspberry Pi Model B. (b) Longitudinal cut (3D model) of the sensing module, showing the 6-sensor array and the 20 mL glass detection chamber. (c) Optical (left), electrical (middle) and opto-electrical sensors schematic.

4. APPLICATIONS

The gels were used as optical and opto-electrical VOC sensors in different versions of the custom-built device.

In the first version, an array of three sensors with distinct composition (the IL and the BP were varied) was exposed to ambient air saturated with individual VOCs. The relative amplitudes of the optical responses were clustered by principal component analysis (PCA) and the 2 first principal components discriminated the 11 tested VOCs (Fig. 3a) [9].

In a second example, a single gel sensor monitored fish freshness at room conditions. The optical signal of the sensor and bacterial growth (monitored by conventional microbiological analysis) were followed over 12 h. A sharp change in signal amplitude at 6 h was in agreement with the start of exponential bacterial growth indicative of fish spoilage (Fig. 3b), thus suggesting the application of this simple and low cost system for fish spoilage detection [13].

To take advantage of the opto-electrical response, one gel film was used in a sensing device and exposed to vapours from mixtures of ethanol in gasoline at different concentrations. When combined, the electrical and optical signals' relative amplitudes correlate with ethanol content (Fig. 3c) using a multiple linear regression model ($p<0.005$) and provide a better estimation than considering the signals individually [9].

Furthermore, by applying an automatic classifier based on Support Vectors Machines (SVM) to 12 morphological features of the optical signals of a single gel, it was possible to classify 11 VOCs with an accuracy of 95 ± 1% (Fig. 3d). Thus, a single gel provided optical fingerprints with enough information for correct VOC identification, a step ahead from the first example (VOC distinction) but with less sensors, which simplifies the sensing aparatus. VOCs from the same chemical class, like ethanol and methanol, were slightly confused as their interaction with the gel is similar.

The robustness of gels as gas sensors is notable as a single gel can be repeatedly exposed to a sequence of 11 different VOCs (13-15% v/v) and still maintain the ability to identify VOCs after 2 months of storage at ambient conditions. The optical responsivity is maintained during 4 years of storage under the same conditions [9]. In previous works that used LC for sensing, inert atmosphere was required to conserve the sensors' properties [11],[14].

5. CONCLUSIONS

The VOC-responsive soft materials described in this work represent a new class of robust, versatile fast-responding biomaterials, combining the gas-sensing potential of liquid crystals and ionogels. Examples of applications with VOC-saturated atmospheres and VOC mixtures were presented. Future work on limits of detection, effect of relative humidity and benchmarking for particular applications will strengthen the potential of the materials. Due to their combinatorial nature, a diversity of gel compositions is feasible and could enable tailoring the gels' selectivity. In addition, the gels can be functionalized with selective moieties and molded in many formats. Finally, the energetic cost of the device is low as the sensors operate at room conditions and the hardware has low consumption. Thus, the gels show potential for developing sensors and sensing arrays of (bio)electronic noses, compatible with miniaturized, portable or wearable devices.

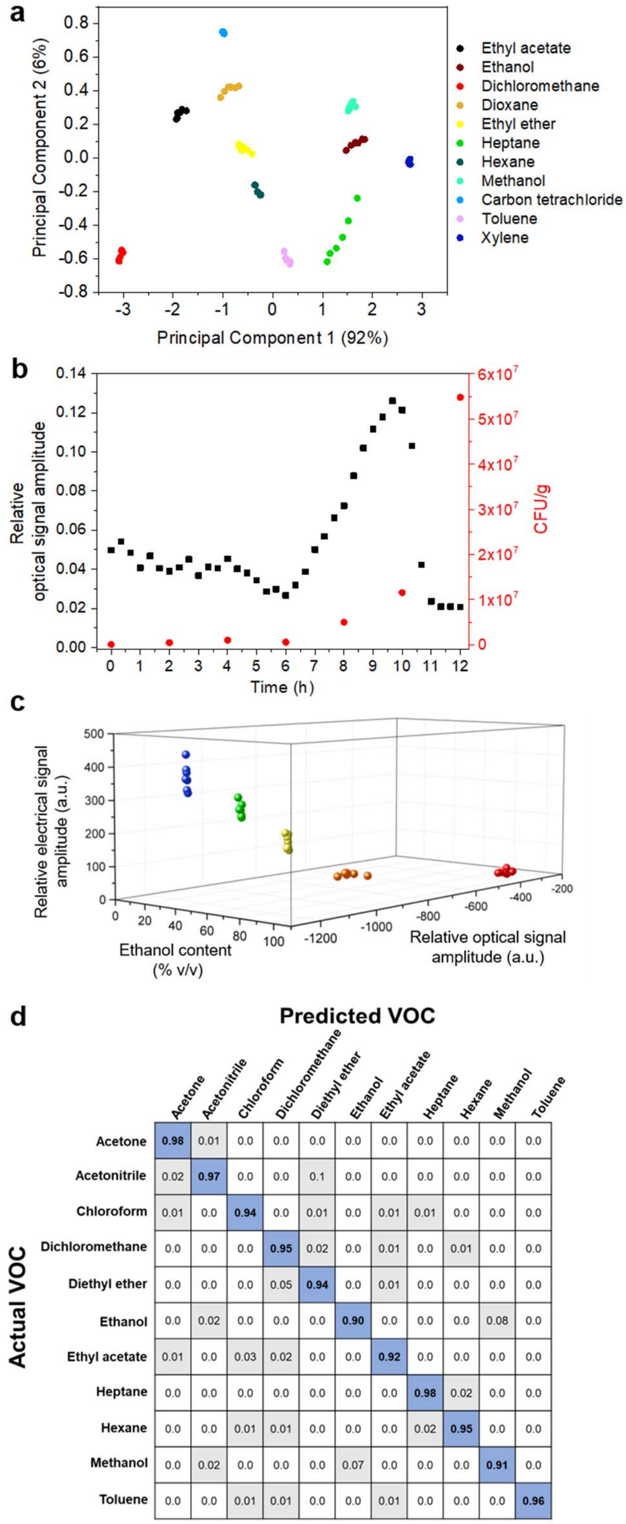

Fig. 3. Application of hybrid gels as optical and opto-electrical gas sensors. (a) Clustering of VOCs by PCA of the relative amplitudes of the optical signals of 3 sensors. (b) Identification of fish spoilage by the change in relative amplitude of a sensor's optical signal and increase in bacterial counts. (c) Electrical and optical response of a sensor as a function of ethanol content in fuel mixtures (d) Confusion matrix representing the performance of VOCs classification using a SVM fed with 12 features of the optical signal of a single sensor.

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