



Chemiresistive ionogel sensor array for the detection and discrimination of volatile organic vapor



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ARTICLE INFO

Article history:

Received 7 November 2013

Received in revised form 11 April 2014

Accepted 8 May 2014

Available online 24 May 2014

Keywords:

Ionogel

Chemiresistive sensor

Electronic nose

VOCs

ABSTRACT

A chemiresistive sensor array consisting of nine different types of ionogels was constructed. The conductivity of each ionogel was very sensitive to stimulations of volatile organic compounds (VOCs). The sensing mechanism of the ionogel was based on the change in ion mobility in response to the absorption of VOCs. This mechanism significantly differed from the currently used chemiresistive sensors, usually relying on the modulation of charge densities. The ionogel sensor can produce a reversible and fast resistance response upon exposure to dosing gases cycled between the VOC sample and N₂. The resistance response of ionogel had a linear relationship with the VOC concentration. Meanwhile, the ionogel sensor displayed selectivity to different types of VOCs because of the specific molecular interaction between ionic liquids and the target organic vapor. A chemiresistive sensor array comprising nine types of ionogel with diverse chemical structures can generate a pattern of cross-reactive responses to a specific vapor, thereby leading to the discrimination of VOCs in air samples using principal component analysis.

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1. Introduction

Volatile organic compounds (VOCs) are common species of indoor air pollutants that majorly threaten human health. Portable sensors integrated with highly sensitive and selective sensing materials are becoming major tools for monitoring VOC concentrations in air samples. Metal oxides [1], carbon materials [2] and conducting polymers [3] are extensively used as sensing elements for VOC detection. However, gas sensors based on a single sensing element usually cannot discriminate different types of VOCs. Electronic noses (e-noses) consisting of multiple sensing elements can mimic the human olfactory system to identify and quantify chemical substances in the vapor phase [4]. Each sensing element on the e-nose is not designed to respond to a single analyte, and instead produces a cross-reactive response. Consequently, a distinct signal fingerprint on the sensor assay occurs upon exposure to a specific analyte. Pattern recognition algorithms [5] can then be used to obtain information on the identity, properties, and concentration of the vapor exposed to the sensor array. One attractive signal transduction mode is the use of chemically sensitive resistors (chemiresistors) as sensing elements of an e-nose system [6,7]. Semiconductor metal oxides [8], surface functionalized gold nanoparticles [9], conductive polymers [10], carbon materials [11],

and their corresponding hybrid materials [12] have been used as sensing elements in the e-nose technology. However, the limited structural diversity of these materials confers difficulty in the selection of multiple sensing elements with high recognition ability.

Ionic liquids (ILs) are organic salts with low melting temperatures. Some important properties of ILs include negligible vapor pressure, thermal stability and non-flammability. Furthermore, the physicochemical properties of ILs can be tuned by modifying the anion cation pair, resulting in diverse structures that open much possibilities [13]. ILs have been widely used in electrochemical sensor because of their high conductivities and wide electrochemical potential windows [14]. Optical sensor based on IL-infiltrated porous silicon (pSi) rugate filter was also developed in our group [15]. The detection of organic vapor is achieved by measuring reflectance peak shift of interferometric reflectance spectroscopy. This peak shift is caused by the condensation of organic vapor in the nanoporous channel of the pSi rugate filter. The utilization of IL can usually improve the selectivity of an electrochemical or optical sensor, due to the strong and specific molecular interactions between ILs and analytes. However, in most of these sensor applications, ILs are used only as electrolytes or adsorbents. In fact, ILs themselves can be good sensing elements because their physical properties (e.g. permittivity and viscosity) are highly sensitive to chemical stimulations [16]. For instance, the viscosity of ILs dramatically changes after mixing with small amounts of organic solvents. Based on this mechanism, quartz crystal microbalance sensors have been constructed using IL as sensing elements for VOC detection [17]. In

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practical applications, direct usage of ILs as sensing material in their liquid form is inconvenient. Therefore, techniques for immobilizing ILs in solid devices while keeping their unique properties are highly demanded [18,19]. Usually, materials resulting from encapsulating or immobilizing ILs in a three-dimensional network are called as ionogel. The properties of ionogel are derived from those of IL and component of solid network, which include organic [20,21], inorganic [22,23] or organic–inorganic hybrid [24]. Meanwhile, the confinement effect of nanopore at host matrix may also severely affect the physicochemical properties of ionogel [25]. In some cases, the physical properties of ILs reportedly become more sensitive to environmental stimulations if the ILs are confined in nanoscale space [26,27]. Therefore, chemical sensors based on ionogel may have higher sensitivity than those based on pure ILs.

The aim of this work is to confirm whether ionogel can be used as chemiresistive sensing material for high sensitive VOC detection. To confine ILs in solid matrices, ionogels were prepared by a sol–gel method, in which different types of ILs were encapsulated in silica gel network. Each type of ionogel showed higher conductivity than their IL-free counterparts. The resistance of the ionogel was found to be highly sensitive to VOC stimulations. Different types of ionogels can produce selective resistance response because of the different molecular interactions between ILs and VOCs. Accordingly, a chemiresistive sensor array consisting of nine types of ionogel was constructed. The cross-reactive sensing ability of the ionogel array enable each type of VOC to produce a unique response pattern on the chemiresistor array. Using principal component analysis (PCA), the species of organic vapors in air sample were then discriminated. To the best of our knowledge, this work was the first to use ionogels as chemiresistive sensing elements. The most significant advantage of this material was its structural

diversity that facilitated the design of a sensor array with enhanced capability to identify or discriminate analytes.

2. Experimental

2.1. Reagents

All ILs used in this work were listed in Table 1. Among them, EPL and P_{6,6,6,14}Triz (purity >98%) were kindly provided by Prof. Wang C. M. in the Department of Chemistry, Zhejiang University. The other types of ILs including BmimNTf₂ (purity ~99%), BmimBF₄ (purity ~99%), BmimPF₆ (purity ~99%), BmimOTf (purity ~98.5%), BmimClO₄ (purity ~98%), BmimCF₃CO₂ (purity ~99%), VOImPF₆ (purity ~99%) were purchased from Lanzhou institute of Chemical Physics, Chinese Academy of Science (CAS). The water content and halide content in each sample were less than 1000 ppm. Tetraethyl orthosilicate (TEOS), methyltrimethoxysilane (MTMS), and formic acid (FA) were purchased from Aladdin Co. (China). Dichloromethane, ethanol, ethyl acetate, hexane, methyl ethyl ketone, toluene, and trichloroethylene were obtained from Sinopharm Chemical Reagent Co. (China). All reagents were of analytical grade and used as received.

2.2. Construction of sensor array comprising ionogel sensing elements

The ionogels were prepared by a non-hydrolytic sol–gel route [28], i.e. a mixture of TEOS and MTMS was added to ILs dissolved in FA solution (FA: TEOS: MTMS: IL molar ratio = 7.8:0.5:1:0.5). A 10 μl mixture of the pre-gel was then dropped onto a patterned ITO electrode or an interdigital electrode. Full gelation occurred after

Table 1
The list of ionic liquids.

Ionic liquids	Structure	Ionic liquids	Structure
BmimNTf ₂ (1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide)		BmimPF ₆ (1-Butyl-3-methylimidazolium hexafluorophosphate)	
BmimOTf (1-Butyl-3-methylimidazolium trifluoromethanesulfonate)		BmimCF ₃ CO ₂ (1-Butyl-3-methylimidazolium trifluoroacetate)	
BmimClO ₄ (1-Butyl-3-methylimidazolium perchlorate)		BmimBF ₄ (1-Butyl-3-methylimidazolium tetrafluoroborate)	
VOImPF ₆ (3-vinyl-1-octyl-1H- imidazol-3-ium hexafluorophosphate)		EPL (N-ethyl piperazinium lactate)	
P _{6,6,6,14} Triz (Tri- hexyl(tetradecyl)phosphonium triazole)			

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