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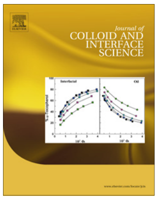

Concentrating materials covered by molecular imprinted nanofiltration layer with reconfigurability prepared by a surface sol–gel process for gas-selective detection

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ABSTRACT

Sensors that recognize molecules are acquired for the comprehensive detection of great many kinds of gases. Adsorbents with high molecular recognition and condensation ability were developed for selective gas sensing with a molecular imprinting technique. Developed adsorbents have multilayer structures consisted of a chemically modified polymer layer on the surface of a substrate covered by a TiO_2 gel monolayer by the surface sol–gel process. Ellipsometry measurements showed that the 6-nm-thick layers deposited on the substrate. Cavities of molecular templates were imprinted on these layers, and thus, the film acts as a molecular gas filter without concentrating ability, which could form specific binding sites for various molecules that confirmed using solid-phase microextraction and gas chromatography–mass spectrometry. Gases were selectively absorbed into an accumulating adsorption layer and other gas molecules were blocked by the nanofiltration. These developed adsorbents enabled effective concentration ability and the filtration of gases or odors. In addition, these filters possess the flexibility to be easily configured with specific surface properties to interact with volatile molecules under appropriate conditions. A successful multiplex filter, imprinted simultaneously on an adsorbent with different sites, was demonstrated.

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1. Introduction

Comprehensive sensing of gases or volatile organic compounds (VOCs) and the identification of great many chemicals are required in various areas of human activity, for example, health, foods, and aromatherapy [1–4]. This might be accomplished by sensing systems inspired by the bio-olfactory system. For example, the artificial construction of a biological odor map, which is formed in the definitely located glomeruli sheet on the olfactory bulb [5–7], should enable the detection and recognition of molecular profiles with high selectivity. Recently, it was observed that glomeruli with similar molecular-receiving properties are located near each other and that the odor map is grouped into clusters with different molecular information, e.g., carboxylic acids belong to cluster A [8–10]. Various molecules are classified into clusters based on molecular structures in the bio-olfaction process [11–13]. On the standpoint of such bio-inspired sensing, the molecular recognition part is indispensable for the discrimination of complex molecular shapes or functional groups. In our previous study, we succeeded in measuring molecular parameters by the sensing devices using conventional adsorbents [14]; however, higher levels of molecular recognition are required to attain the bio-olfaction sensing system.

The molecular imprinting technique (MIT) has gained considerable attention as an attractive synthetic approach for preparing host compounds with high molecular recognition of imprinted template molecules [15–18]. These molecular-recognizing sites consist of specific subsite areas formed by hydrogen bonding interactions among complementary functional groups of polymers and templates [19]. The specific interactions can be reversible covalent and non-covalent [20]. The shape and spatial arrangement of functional groups, complementary to templates, are imprinted on polymers [21]. Molecular imprinting polymers (MIPs) with specific binding sites exhibit high selectivity and sensitivity for templates [19]. Moreover, MIPs enable the selective detection of organic molecules and the microfiltration of others [22]. Therefore, MIPs were actively studied for applications such as chromatographic separation [23], solid-phase extraction (SPE) [24], and chemical sensors [25].

Conventional MIPs still have major challenges with respect to the adsorption of gases. To a great extent, the adsorbability is dependent on the properties of constituent elements of MIPs and there exists material limitation of monomers and cross-linkers [15]. Non-specific adsorption occurs not only on recognition sites but also on matrix polymer parts. In addition, it is difficult to also

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form reconfigurable MIPs that are complementary to various templates because of strong immobilization. Therefore, MIPs are also inferior in terms of condensation and flexibility. Moreover, although the MIP filters using membrane technology and MIT become increasingly attractive for the separation of special template molecules and others from various compounds [21], the development of molecular filters with nanometer thicknesses is difficult by polymerization with a highly cross-linked polymeric network.

In the present study, molecularly imprinted filtering adsorbents (MIFAs) were developed for highly gas-selective detection [26]; hence, MIFAs are a modified MIP filter on the surface of adsorption materials, which serve as a condensing layer to concentrate molecules. Fig. 1 shows the design of the layered MIFA structures. Polydimethylsiloxane (PDMS) was selected as concentrating substrate for the MIFAs in this study. Because PDMS is used as a highly adsorbing layer in solid-phase microextraction (SPME), MIFAs have high condensation ability by highly gas permeability properties of PDMS. Monolayers of titanium oxide (TiO_2) gels could be assembled on a PDMS substrate using the surface sol–gel process [27,28] for the surface modification of MIP filters on PDMS. Then, poly (acrylic acid) (PAA)/template complex was chemically bound to the surface TiO_2 layer [29,30]. Therefore, The PDMS surface was covered by a TiO_2/PAA layer of a few nanometers in thickness. In the adsorption mechanism of the MIFAs, it is thought that measured VOC gases or odors are concentrated into accumulating adsorption layers after sinking into molecular cavities and then the VOC molecules pass through MIP filters.

Specific binding sites of MIPs were formed based on intermolecular forces between PAA matrix or Ti–O layer and template molecules. The imprinted sites were stabilized on the TiO_2 surface by the surrounding titania film network [31]. In particular, in the case of carboxylic acids, the stable carboxylate site was strongly formed by carboxylate bonding between Ti–O and the carboxylic group. Then, the hydrogen bonding sites of the MIP filters were generated in the PAA film by the interaction between PAA and template molecules [32,33]. These sites were thought to maintain complex areas that are complementary to templates. The hydrophobic cavities that correspond to carbon chains of the templates were also prepared, because the force of about 6.9 kJ/mol weakly acts between CH units; however, total van der Waals forces become strong by long carbon chain composed of PAA matrix [34]. The specific binding sites must be constituted of these types of sites [31], as shown in Fig. 2.

These nanofilters of MIFAs possess high affinity and selectivity of MIPs toward the templates. Therefore, MIFAs and the technique introduced in this study are specific in following ways, comparing to other MIP materials. First, ultrathin MIP filters can chemically be stabilized on a variety of devices, e.g., electrodes and metal nanoparticles, other than adsorbent materials. Second, structurally identical molecules can be concentrated into accumulating adsorption layers through an MIP filter. Therefore, MIFAs exhibit a molecular-sieving effect and high condensation ability. Third, MIFAs have high extensibility because functional materials suited to target VOCs and odors were adopted from many adsorbents as concentrating layer. Fourth, non-specific adsorption can be avoided effectively by using the filter having nanometer thickness. Finally, the flexible MIP filters also possess reconfigurable and multiplex properties, i.e., multiple sites for the interaction with different molecules can be provided, and hence, different selective properties can be designed to the filter.

The purpose of our research is to develop a nanofilter that has selective recognition sites in molecular level. The molecular nanofilter is a potentially functional material that can be used in the discrimination of complex molecular shapes and functional groups of chemical molecules. The developed filters should have high performances in various application fields, such as sensors, separations, and therapeutics. In addition, developed filters are thought to be generally available in the area of surface science and colloid because MIP filters can chemically be stabilized on a variety of materials as nano-particles.

2. Experimental

2.1. Chemicals

The following chemicals were purchased from Wako, Japan: PAA (MW = 5000), tianium (IV)-n-butoxide ($Ti(O\text{-}n\text{-}Bu)_4$), reagents (propanoic acid, hexanoic acid, heptanoic acid, octanoic acid, 2-hexanone, 2-heptanone, 3-octanone, 2-nonanone, propanal, pentanal, heptanal, 1-heptanol, acetophenone, anisole, cresol, and

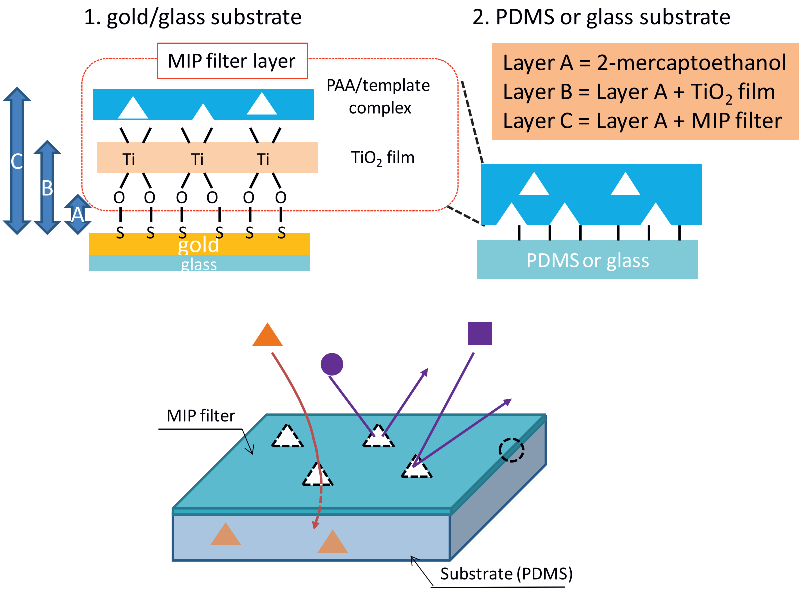

Fig. 1. Schematic illustrations of the sandwich structure of MIFAs, where the MIP filter was modified on the substrate. Templates were selectively concentrated on PDMS through the MIP filter.

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