Title: Cyclodextrin-Based Chemical Microsensors for Volatile Organic Compounds (VOCs)

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Cyclodextrin-Based Chemical Microsensors for Volatile Organic Compounds (VOCs)

DeQuan Li*

Abstract
This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). This project addressed the development of surface-acoustic-wave (SAW)-based chemical sensors for remote, real-time sensing in air, groundwater, and possibly soil, of chlorinated and aromatic hydrocarbons using innovative molecular self-assembly techniques. Our goal is parts per billion (ppb) sensitivity to specific aromatic and chlorinated hydrocarbons using cyclodextrin as the selective layer of a SAW-based mass sensor. We have demonstrated that SAW sensors can differentiate between compounds with similar composition, structure, and polarity. These efforts, however, can be enhanced by using sensor arrays and smart data processing systems. Secondly, ionic interactions provide a convenient way to fabricate thin films for sensor applications. The potential of these thin films for sensor applications is currently being evaluated.

Introduction

At Los Alamos National Laboratory (LANL), advanced work continues in constructing superior chemical sensors based on tailoring the surface chemistry of the sensing layer on surface-acoustic-wave (SAW) devices. Such sensors are desired for cost-effective environmental monitoring, site remediation, and industrial process characterization. Two versatile families of organic "bucket" molecules known as cyclodextrins and calix[n]arenes have attracted much attention recently because of their inclusion chemistry (see Figure 1). These receptors can be further functionalized and then reacted with inorganic transducer surfaces or functionalized organic transducer surfaces. The surface-attached nanometer-sized host molecules can be predominantly aligned upward and given a locally modified chemical environment suitable for hosting complex volatile organic compounds (VOCs). The inside of the host cavity exhibits hydrophobic properties and, depending on the variety and functionalization, has the size and chemical environment to readily incorporate specific VOCs via host-guest interactions. The sensor mechanism in this case is based on a novel concept of noncovalent interactions—hydrophobic affinity, hydrogen bonding, and inclusion force. Because these interactions are weak, the resulting sensor is completely

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Figure 1. Chemical structure of α-cyclodextrin; β-, γ-cyclodextrins have one and two more glucose units in the rings, respectively (α: \(d = 4.7-5.2 \ \text{Å}\); β: \(d = 6.0-6.5\); γ: \(d = 7.8-8.5 \ \text{Å}\)), which form a hydrophobic cavity able to include organic vapors.

reversible—the VOCs quickly clear from the sensor after their concentrations are reduced.

We have employed a strong linkage to attach host molecules to oxide surfaces terminated with hydroxyl groups. The asymmetric host molecules that have been used to make SAW transducers include

- α-cyclodextrin dodeca(20,30)benzoate (CDCB),
- β-cyclodextrin tetradeca(20,30)benzoate (CDTB),
- β-cyclodextrin tetradeca(20,30)acetate (CDTA),
- γ-undecylcalix[4]resorcinarene (UCR), and

Calixarenes and resorcinarene are synthetic, whereas cyclodextrins are chiral, toroidal-shaped enzymatic products formed under the catalysis of enzyme cyclodextrin transglycosylase on hydrolyzed starch (see Figure 1). The molecular-engineered cyclodextrin or calixarene host monolayers have a sensitivity of 5 ppm to perchloroethylene (PCE), based on a noise level in the sensor frequency of 5 Hz. The interactions between hosts and guests can be optimized by proper alignment, use of a lipophilic cavity, and functionalization of the upper rim. Monolayers of β-cyclodextrin derivatives are also more sensitive to PCE; the response to PCE is ~5 and ~20 times higher than the responses to toluene and chloroform, respectively.
The sensor responses of these SAW devices are typically real-time, reversible, and rapid (~sec). For sensitive thin-film coatings, the SAW sensors can show saturation at high-organic-vapor partial pressures. However, the sensor also exhibits a linear response within its dynamic concentration range, especially at low concentrations. Typical cyclodextrin-monolayer-sensor responses to VOC partial pressures at 15.0 ± 0.1°C gave frequency shifts of 8.0 kHz or less, corresponding to approximately one monolayer or smaller amounts of the VOC. This suggests an average of one or less analyte molecules per surface-attached monolayer of host molecules. As expected, the sensor responses (Δf) increased almost linearly with the cyclodextrin thin-film thickness; ultrahigh-sensitive VOC sensors were successfully demonstrated in this manner.

**Importance to LANL’s Science and Technology Base and National R&D Needs**

The development of new chemical sensors is critical to the success of laboratory programs in environmental restoration, waste management, advanced manufacturing technologies and counter-proliferation. Problems associated with materials compatibility and durability, species selectivity, sensitivity, and reversibility are at the heart of current chemical sensor limitations and this research effort could lead to the development of an entirely new class of chemical sensors that impact a wide range of problems associated with environmental cleanup, environmental compliance, waste minimization, environmentally conscious manufacturing, and counter-proliferation.

**Results and Discussion**

As previously shown (see Publications), it is possible to produce individual sensors with high sensitivity. We have also demonstrated the feasibility of making sensor arrays with the present approach. Sensing layer fabrication, however, is still complicated, and we have been focusing on simplifying thin film formation with this one-year project.

Our previous approach has been to use covalent bonds to produce thin films with superior stability. The formation of covalent bonds, however, is a slow process and hence the speed-limiting step in multilayer fabrication. On the other hand, ionic interactions have fast kinetics. Based on these considerations, our strategy is first to functionalize cyclodextrin with covalently bonded chemical moieties and then use ionic bonds to assemble them into multilayer thin films.
In order to generate multiple ionic charges on the rim of cyclodextrin buckets, we reacted cyclodextrin with POCl₃ followed by hydrolysis (see reaction below). The resulting materials are cyclodextrin buckets with multiple phosphonates that are negatively charged: –14 charges for the primary side and –28 charges on the secondary side of β-cyclodextrin.

\[
\begin{align*}
\text{HO} & \quad \text{POCl₃} \\
\text{HO} & \quad \text{PO₃²⁻} \\
\end{align*}
\]

The negatively charged cyclodextrins were then stacked on the surfaces of 400 MHz SAW devices with poly(dimethyl diallyl)ammonium as a counter ion (see Figure 2). Because of multiple ionic interactions, the resulting bond strength is equivalent to a covalent bond. However, the procedure for assembling these multilayers is greatly simplified.
Sensor measurements were performed on the following chlorinated compounds: chloroform (CF), carbon tetrachloride (CT), trichloroethane (TCA), and perchloroethylene (PCE). We chose these compounds because they have similar chemical properties and structures: SAW sensors that can differentiate between compounds that closely resemble each other can be used to differentiate between any chemical vapors. The results are summarized in Figure 3, which suggests that it is possible to differentiate PCE and CT from chloroform and TCA. The responses for chloroform and TCA are too close to each other for the present sensor to identify them accurately at unit concentrations.

In the host-guest detection scheme, sensor selectivity depends on optimum chemical or physical interactions between the analyte and the host cavities; such interactions involve good matching of polarity, size, and structure. The cyclodextrin multilayers show good selectivity for a group of organic template analytes chosen for their similar structures and polarities to probe the cavities of the host compounds (Figure 3).
Figure 3. Bar graph showing that the sensitivity of the multilayer sensor to various chlorinated chemicals: chloroform (CF), trichloroethane (TCA), perchloroethylene (PCE), and carbon tetrachloride (CT).

Publications


