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CYCLODEXTRIN-BASED SURFACE ACOUSTIC WAVE CHEMICAL  
MICROSENSORS

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## CYCLODEXTRIN-BASED SURFACE ACOUSTIC WAVE CHEMICAL MICROSENSORS

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## ABSTRACT

Cyclodextrin thin films were fabricated using either self-assembled monolayer (SAM) or sol-gel techniques. The resulting host receptor thin films on the substrates of surface acoustic wave (SAW) resonators were studied as a method of tracking organic toxins in vapor phase. The mass loading of surface-attached host monolayers on SAW resonators gave frequency shifts corresponding to typical monolayer surface coverages for SAM methods and "multilayer" coverages for sol-gel techniques. Subsequent exposure of the coated SAW resonators to organic vapors at various concentrations, typically 5000 parts per millions (ppm) down to 100 parts per billions (ppb) by mole, gave responses indicating middle-ppb-sensitivity (~50 ppb) for those sensor-host-receptors and organic-toxin pairs with optimum mutual matching of polarity, size, and structural properties.

## I. INTRODUCTION

Chemical microsensors are desired for cost-effective environmental monitoring, site remediation, and industrial process characterization,<sup>1</sup> and are expected to play a growing role in these applications. The analyses of volatile organic compounds (VOCs) are currently performed with standard analytical instruments such as gas chromatography and mass spectrometry. By integrating a surface acoustic wave (SAW) measurement platform with a selective sensing layer, a desired chemical microsensor is constructed, which provides some of the functionality of analytical instrumentation, but with drastically reduced cost, size, and power consumption.

There has been numerous work on SAW device fabrications not only for chemical sensors but also for communication devices such as frequency filters and cellular phones. Little, however, has been done on engineering the selective sensing layers. We focus here a novel approach to construct new host receptors as a sensing layer on SAW devices using innovative molecular self-assemblies and sol-gel techniques.

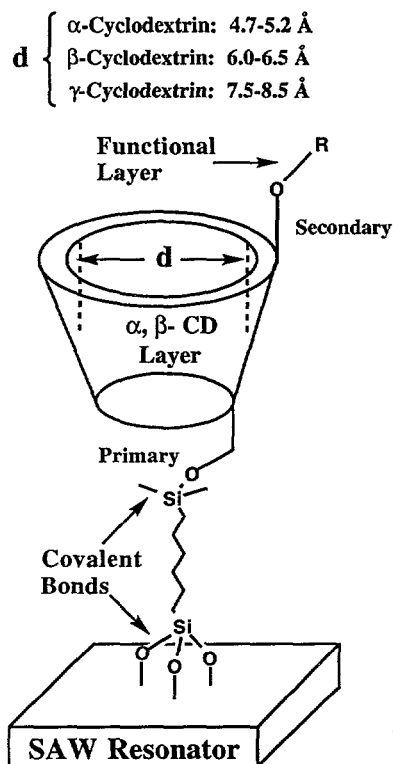
## II. RESULTS AND DISCUSSIONS

Cyclodextrins are chiral, toroidal-shaped enzymatic products formed by the action enzyme cyclodextrin transglycosylase on hydrolyzed starch. They contain  $m = 6$  to 12 glucose units bonded together through  $\alpha$ -(1,4)-linkage, whose characteristic sleeve-like-cavity size and shape are defined by  $m$ . The three smallest homologs,  $\alpha$ - ( $m = 6$ ),  $\beta$ - ( $m = 7$ ), and  $\gamma$ - ( $m = 8$ ) cyclodextrins, are commercially available. These host cavities exhibit hydrophobic behavior; depending on the variety, they have the size and chemical environment to readily incorporate specific chemical agents or target organics through "host" and "guest" interactions. Furthermore, the polarity and the size of the cyclodextrin's cavity can be chemically modified and structurally tuned to further enhance molecular recognition ability.

The self-assembled monolayers of cyclodextrin receptors on SAW surfaces were prepared by reacting cyclodextrin derivatives with a bifunctional bis(1,6-trichlorosilyl)hexane) (BTCSH) derivatized oxide surface to create covalently bound sensing layer with tailored selectivity as shown in Scheme I.<sup>2</sup> The surface attached nanometer-sized host molecules are predominantly aligned upward<sup>3</sup> and endowed

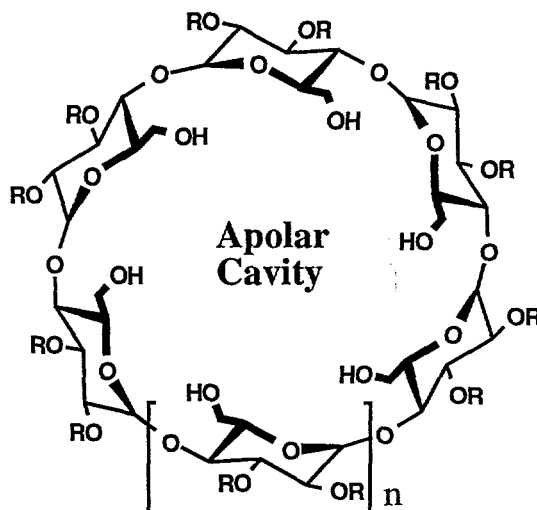
with a locally modified chemical environment to complex volatile organic compounds.

Scheme I



Using efficient molecular engineered cyclodextrin host monolayers, we have achieved sensitivity comparable to that of thicker polymer spin-casted or spray-coated films.<sup>4</sup> The optimized interactions between hosts and guests are attributable to the proper alignment, lipophilic cavity, and functionalization of the upper rim. The asymmetric host molecules used in this study include  $\alpha$ -cyclodextrin dodeca(20,30)-benzoate (1),  $\beta$ -cyclodextrin tetradeca(20,30)-benzoate (2),  $\beta$ -cyclodextrin tetradeca(20,30)-acetate (3). Host compounds 1 and 3 were prepared according to the reported literature procedures;<sup>5</sup> whereas, host compound 2 was synthesized by treating  $\beta$ -cyclodextrin with *t*-butyldimethylsilyl chloride followed by benzoation reaction using benzoyl chloride in pyridine. The host monolayer thin films were prepared by exposing the cleaned substrates to the vapor of 1,6-bis(trichlorosilyl)hexane by bubbling argon through a trap-bubbler-trap system at 150 mL/min at 70 °C. The silane derivatized substrates were then immersed in the ~1.0-5.0

mM corresponding cyclodextrin solutions for about 2 hrs at room temperature to allow the formation of self-assembled host monolayers. The sol-gel precursors were synthesized by reacting cyclodextrin with isocyanatopropyltriethoxy-silane in pyridine at 75 °C for 48 hours, followed by removing of the solvent and redissolving the sol-gel precursors in DMF. The sol-gel films were prepared by simply immersing the corresponding SAW devices in the above 10 mM sol-gel precursor solution in DMF at room temperature for two days.



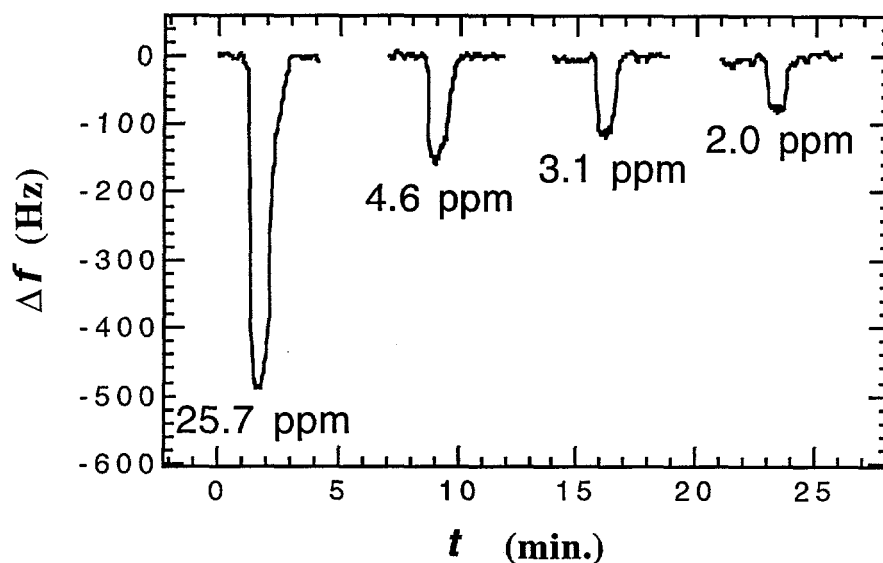
- 1:  $R = -\text{COC}_6\text{H}_5$ ,  $n = 1$   
 2:  $R = -\text{COC}_6\text{H}_5$ ,  $n = 2$   
 3:  $R = -\text{COCH}_3$ ,  $n = 2$

SAW resonators (200 MHz) were used to measure sensor response to organic analytes.<sup>6</sup> The phase velocity of this acoustic wave—and therefore the resonant frequency of the device—is a sensitive function of the physical properties of any contacting materials. In the present case of thin, nonconductive thin films, electrical and viscoelastic effects are minimal and the resonant frequency shift ( $\Delta f$ )<sup>6d</sup> depends mainly on the mass loading per unit area ( $\Delta m/A$ ) of the sensing monolayer<sup>7</sup> and any adsorbed vapors according to eq. (1), where  $K = 1.3 \times 10^{-6} \text{ s} \cdot \text{cm}^2/\text{g}$ .

$$\Delta f = -K f^2 \frac{\Delta m}{A} \quad (1)$$

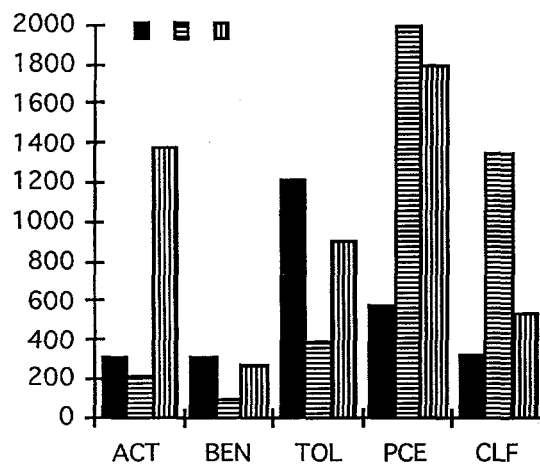
Figure 1 shows real-time reversible, rapid (~sec) sensor response for a cyclodextrin sol-gel film to acetone at a concentration range from 25 ppm to 2 ppm. Over five orders of vapor concentrations (~5,000 ppm-50 ppb), a nonlinear behavior was observed at extreme organic vapor

partial pressures; whereas sensor exhibits a linear response within a narrow concentration range, especially at low concentrations. For xylene and perchloroethylene, the vapor concentrations were traced as low as ~50 ppb.



**Figure 1.** The cyclodextrin-coated, surface-acoustic-wave-based sensor responds to 1-minute-wide acetone pulses at the particular concentrations shown. The film was prepared from  $\beta$ -cyclodextrin with 14 equivalent amount of isocyanatopropyltriethoxysilane on both primary and secondary sides.

Sensor selectivity depends on optimum chemical or physical interactions between the analyte and the sensing layer such as mutual matching of polarity, size, and structural properties. The cyclodextrin monolayers show appreciable selectivities within a group of organic template analytes chosen for their variety of structures and polarities to probe the cavities of the host compounds (Figure 2). The observed selectivities are expected, as the inclusion complexes of phenyl units into  $\alpha$ -cyclodextrin and the optimum fit of perchloroethylene into  $\beta$ -cyclodextrins are well-documented by UV-vis,<sup>8</sup> NMR,<sup>9</sup> and X-ray crystallography<sup>10</sup> in the literature. The sensor each shows a distinct set of relative responses among a group of analytes, attributable to inherently different local host chemical environments. Conversely, a judicious assortment of sensing layers in an array of microsensors can be used to provide a unique characteristic pattern of responses for each compound. For instance, the response of chloroform as illustrated in Figure 2 to an array



**Figure 2.** The bars represent the distinct responses (frequency shifts in Hz) of 5 volatile [Acetone (ACT), Benzene (BEN), Toluene (TOL), Perchloroethylene (PCE), and Chloroform (CLF)] organic compounds to 3 different host monolayers (from left to right 1, 2, and 3).

of microsensors coated with monolayers of host 1, 2, and 3 is a sharp peak. The same sensor array responds to toluene with a "doublet," and each compound has its own characteristic response to this sensor array. VOCs which closely resemble each other, for instance, benzene and toluene, yield similar patterns.

#### IV. CONCLUSION

To summarize, we have successfully synthesized cyclodextrin-based monolayers and sol-gel films which were shown to have ppm-ppb sensitivity to targeted organic analytes. Pattern recognition with an array of microsensors appears to be a feasible approach for identifying a particular VOC.

#### ACKNOWLEDGMENTS

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