# Chapter 24
# Materials Design of Sensing Layers for Detection of Volatile Analytes

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## ABSTRACT

*The authors developed highly sensitive sensing layers for detection of Volatile Organic Compounds (VOCs) by using polymeric nanomaterials. In this chapter, they describe their recent progress on the design of polymeric sensing layers for the chemical sensors. The nanostructures of polymeric sensing layer strongly influenced the sensitivity and selectivity for VOCs sensings.*

## INTRODUCTION

We are constantly exposed to health and safety hazards as a result of dynamic and unpredictable conditions. On-site and real-time analyses of ambient information on factors such as sounds, colors, and odors provide us with situational awareness to manage these hazards. Among the ambient factors, odorants are detected and discriminated though olfaction and the physicochemical properties of odorants induce specific odor sensations by selective binding with odorant receptors in the nasal cavity. The chemical features of the odorants activate multiple receptors and all of the signals are sent to the brain as activation patterns to recognize a specific group or feature of the target odorant.

Artificial electronic nose systems have been developed for the detection of volatile odorants. These systems mimic the mammalian olfactory system by producing sensing patterns of cross-responsive sensor arrays. The systems comprise a chemical sensor array together with an interfacing electronic circuitry, as well as a pattern recognition unit that acts as a signal processing system. The chemical sensor arrays are capable

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of converting chemical information into an output signal and each sensor in the array can generate different signals in response to the concentration and the specific interaction with target odorants. Target odorants cannot be identified from the response of a single sensor element. A response pattern from multiple sensors in the arrays can provide a fingerprint that allows classification and identification of the odorant. To yield the sensing patterns requires a variety of sensing layers with different responses for odorants.

Mass sensors have been applied to chemical sensing in the electronic nose systems by the use of various sensing materials. When VOCs are captured within the sensing layers on the mass sensors, the sorption amounts can be monitored by resonant frequency shifts of the sensors. The determination of weight changes is directly related to the interactions between the sensing layers and target compounds. Quartz Crystal Microbalances (QCMs) have been widely used as the platform for mass sensing by the deposition with the sensing layers. The resonance frequency has been proven to decrease linearly upon the increase of weight on the QCM electrode in a nanogram level. Recently, silicon resonators such as microcantilevers and microdisks have come to be expected to provide an alternative platform for mass sensors. The microfabrication processes of silicon makes it possible to significantly downsize of sensor arrays and integrate various components onto one chip.

We have developed highly sensitive sensing layers for detection of VOCs by using nanomaterials such as the polymer thin films, the dense surface of polymer brushes, and sterically protected metal complexes. In this chapter, we describe our recent progress on the design of the sensing layers for the chemical sensors. The sensitivity, selectivity, and responsibility for VOCs sensing systems depend on the chemical structure of polymeric sensing layers and microenvironment around the receptor molecules.

## POLYMER-BASED RECOGNITION LAYERS

### Polymer-Coated QCM Sensor Arrays

Polymers have been used as sensing layers owing to their great design flexibility. The polymers offer an advantage as a sorbent coating for the detection of analytes by using QCM sensors because they provide specific interactions with analytes as well as form stable thin films (Matsuguchi & Ueno, 2006; Kikuchi, Tsuru, & Shiratori, 2006; Zeng, et al., 2007; Si, et al., 2007; Ichinohe, Tanaka, & Konno, 2007; Matsuguchi, et al., 2008; Ju, et al., 2008; Ayad & Torad, 2009; Du, et al., 2009; Baimpos, 2010; Wang, et al., 2010; Nomura, et al., 2010). Polymers can offer enhanced sensitivity and a real-time response in the QCM sensor systems. The responses of polymer-coated QCM sensors to exposure to VOCs were studied under various operational conditions and were also applied to the detection of VOCs by the response analyses of QCM sensor arrays.

The chemical structures of four polymers are shown in Figure 1a. Four polymers, polystyrene (PS), polybutadiene (PBD), poly(acrylonitrile-*co*-butadiene) (PAB), and poly(styrene-*co*-butadiene) (PSB), were deposited onto the gold electrode of 9 Mz QCMs by the spin-coating method. The SEM image of the PBD-coated QCM shows a smooth and uniform surface. The thickness of the PBD layer was 400 nm as observed in the cross-sectional SEM image shown in Figure 1b. The deposition of polymer films on QCMs induced the frequency decrease at approximately 7000 Hz. Using the Sauerbrey equation (Sauerbrey, 1959), this frequency decrease is equivalent to a mass coating of 7400 ng. The thickness of the deposited polymer films is about 400 nm, estimated from the weight obtained from the frequency decrease, the density of polymers, and the area of the electrode. The estimated thicknesses agree with those observed from the SEM images.

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