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Volatile Organic Compound Sensing by Gold Nanoparticles Capped with Calix[4]arene Ligand

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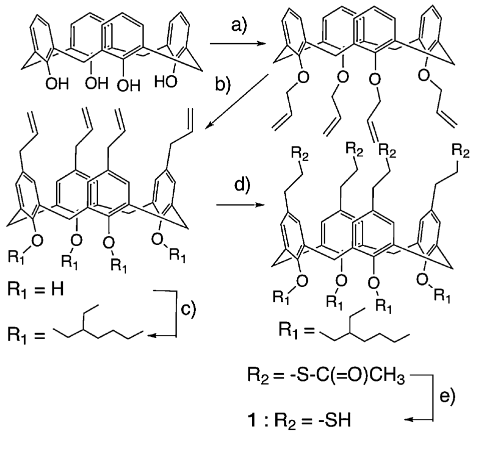
Gold nanoparticles capped with calix[4]arene ligands have been designed and synthesized for highly sensitive and selective VOC sensing. Mass sensors coated with porous nanoparticle films displayed a good response toward toluene gas.

Chemical sensors for volatile organic compounds (VOCs) have attracted special attention due to their potential applications in the fields of environmental and health monitoring.[1] Numerous sensing materials have been developed to convert the chemical features of a target VOC into output signals. Intermolecular interactions between host sensing materials and VOCs enable the selective capturing of the VOC within the sensing layers on sensors and the selective capturing of VOC provides specific output signals from the chemical sensors. The selective capturing of VOCs within the sensing materials on a sensor platform induces the generation of output signals, such as optical, resistance, and mass changes.[2] When VOCs are captured within the sensing materials on mass sensors, the amount of adsorption can be monitored by focusing on the resonant frequency shifts of the sensors. The determination of the mass changes is directly related to the interactions between the sensing materials and the target VOCs.

Quartz crystal microbalances (QCMs) have been widely used as mass sensors by the deposition of sensing materials.[2] Various organic sensing materials have been used as molecular recognition layers because of their great design flexibility. However, the viscoelastic property of organic sensing materials strongly contributes to the resonance properties of QCMs. In addition, the diffusion of VOCs into the sensing films depends on the packing density of the sensing materials. The combination of metal nanoparticles with organic compounds has been investigated to avoid these limitations of organic sensing materials.[3–9] Nanoparticle films allow for the propagation of acoustic waves onto the QCMs as well as the smooth diffusion of analyte molecules within the films. Furthermore, the sensing materials can interact with the analyte molecules at the surface of nanoparticles.

Calix[4]arenes have been investigated for use as molecular receptors because of their shape-persistent hydrophobic binding pockets in their cone conformation.[10] Swager et al. reported on the selective sensing of xylene isomers using a resistance sensor based on single-walled carbon nanotubes wrapped with calixarene-substituted polythiophenes.[11] We also expect the selectivity of calix[4]arenes for aromatic VOCs. We report herein on a mass sensor deposited with Au nanoparticles capped with calix[4]arenes that exhibits high selectivity and sensitivity for VOC sensing. Gold nanoparticles capped with calixarene ligands were synthesized and investigated for their molecular recognition properties.[12–15] However, there are no papers on the selective sensing of gaseous molecules by using the π-electron-rich cavities of calixarenes adsorbed to the surface of Au nanoparticles.

Thiol-terminated ligand **1** was synthesized from calix[4]arene according to Scheme 1. The phenols in calix[4]arene reacted with allyl bromide in the presence of NaH in dry DMF and a Claisen rearrangement was carried out in the presence of *N*,*N*-dimethylaniline leading to the upper rim functionalized calixarene.[16] The remaining four phenol groups at the lower rim of the calixarene reacted with 2-ethylhexyl bromide. The double bonds were converted into thioacetyl groups by reacting with thioacetic acid in the presence of azobisisobutyronitrile (AIBN). The thiol-terminated ligand **1** was synthesized by the hydrolysis of the thioacetyl groups. Compound **1** possesses four thiol groups, which serve as an anchor to bind **1** to the gold nanoparticle surface. The ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **1** shows the presence of two doublets corresponding to the methylene bridges of the macrocyclic skeleton, suggesting that calixarene molecules exist in the cone formation.[15] The intramolecular rotation of the benzene rings in the macrocyclic annulus is blocked by the bulky 2-ethylhexyloxy substituents in the lower rim. Monomeric **2** (Chart 1) was prepared to investigate the aromatic cavity effect on the selectivity in VOC sensing. All the synthesized compounds were characterized by ^{1}H NMR, FT-IR, and MALDI-TOF-MS.



Scheme 1. Synthesis of calixarene ligand **1**. Reagents and conditions: a) Allyl bromide, NaH, DMF; b) *N*,*N*-dimethylaniline; c) 2-ethylhexyl bromide, K_2CO_3, DMF; d) CH_3COSH, AIBN; e) HCl.

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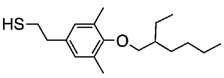

Chart 1.

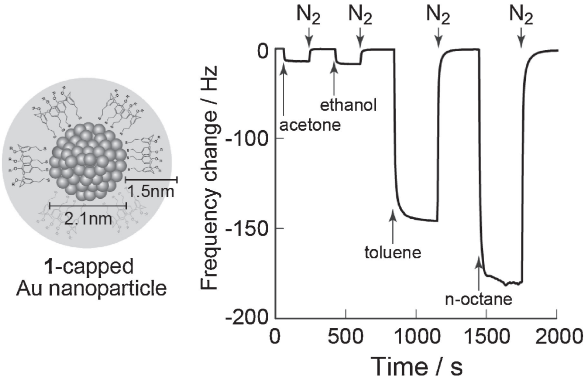

Figure 1. Frequency changes of QCM sensors coated with 10 µg of **1**-capped Au nanoparticles exposed to 2000-ppm VOC vapors measured at 20 °C. The inset is a schematic illustration of **1**-capped Au nanoparticle. The size of the Au nanoparticle and the thickness of calixarene layer were estimated from a TEM image and a computer-generated molecular model, respectively.

Surface-capped Au nanoparticles were prepared by reduction of $HAuCl_4$ with $NaBH_4$ in the presence of **1** or **2**.[17] **1**- and **2**-capped Au nanoparticles can dissolve in many organic solvents such as tetrahydrofuran (THF), CH_2Cl_2, toluene, and DMF. The average diameter and standard deviation of **1**-capped Au nanoparticles are 2.1 and 0.5 nm as determined from the transmission electron microscopic images (Figure S1 in Supporting Information; SI[22]). Absorption spectrum of **1**-capped Au nanoparticle in THF displayed a surface plasmon band at around 520 nm, also suggesting the formation of small Au nanoparticles (Figure S2, SI[22]).[18] Thermogravimetric analyses (TGA) of **1**- and **2**-capped gold nanoparticles showed weight losses of 37.3 and 38.2% at 550 °C, indicating that the density of cone-shaped **1** on the surface of Au nanoparticles is slightly lower than that of monomeric **2**. The numbers of ligand on Au nanoparticles can be estimated from the average diameter of Au nanoparticles determined from TEM images and the weight losses from TGA. The numbers of ligand are estimated to be 29 and 150 for **1**- and **2**-capped Au nanoparticles, respectively.[19] The thiol terminates in **1** were bonded to the Au nanoparticles and formed a dense packing of calixarenes onto the surface of Au nanoparticles (Figure 1).

Au nanoparticle films were deposited onto the surface of QCMs by spin-coating 1 wt % THF solutions of **1**- or **2**-capped Au nanoparticles. Packing Au nanoparticles can form a porous structure with a large active surface area. When a 10 mg of nanoparticle film is deposited on the surface of QCMs (0.19 cm^2 gold electrode area), the nanoparticle film has roughly 50 times the surface area of comparable nonporous films. QCMs coated with **1**- and **2**-capped Au nanoparticles were set into a temperature-controlled measurement chamber and the sensing properties of these modified QCMs (AT-cut quartz crystal, 9 MHz operation frequency) were investigated by monitoring the frequency changes when the films were exposed to toluene, *n*-octane, acetone, and ethanol vapors.[20] These solvents have comparable vapor pressures and represent analytes ranging from nonpolar to polar VOCs. All the measurements were conducted at a sensor temperature of 20 °C to avoid any temperature-dependent frequency changes. Figure 1 shows the time courses of the sensor responses of the QCMs coated with **1**-capped Au nanoparticles responding to exposure to 2000-ppm VOC vapors. The QCMs responded with a decrease in the resonant frequency within 30 s of switching the carrier gas flow from pure nitrogen to VOC vapor. The decrease in resonant frequency indicates an increase in the film's mass through the adsorption of VOCs within the nanoparticle films. When the carrier gas was changed to pure nitrogen, the frequency returned to the original value within 20 s, which indicates fast adsorption and desorption processes of the VOCs in the nanoparticle films. The reversibility and repeatability of the sensor responses were confirmed by applying the VOC vapors for three consecutive exposures in each experiment.

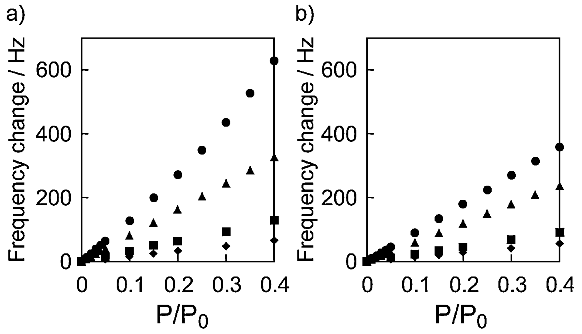

Figure 2. Vapor response isotherms of QCM sensors coated with 10 µg of (a) **1**- and (b) **2**-capped Au nanoparticles to toluene (●), *n*-octane (▲), acetone (■), and ethanol (□).

The response isotherms for the QCMs coated with **1**- and **2**-capped Au nanoparticles for four VOCs are shown in Figure 2. Both nanoparticle films display linear dependencies of the adsorption amount for the four VOCs on the VOC's vapor pressures P/P_0. The slope differences of the P/P_0 dependence are due to the differences in chemical affinity between the nanoparticle film and VOCs as well as the molecular properties of the VOCs such as their molecular volume. The slope for the toluene sensing in the QCM coated with **1**-capped nanoparticles is 2.2 times that compared to that with **2**-capped nanoparticles, indicating a higher sensitivity of **1** for aromatic toluene. The differences in molecular interaction of the VOCs at the surface of nanoparticles affected the sensor sensitivity.

The QCM responses can be increased by increasing the amount of sensing films. However, the lower resonance propagation of sensing films leads to unstable oscillation due to the contribution of the viscoelastic effect of coated materials. The QCMs with different film thicknesses of **1**-capped nanoparticles and 5,11,17,23-tetra(*tert*-butyl)-25,26,27,28-tetrakis(2-ethylhexyloxyl)calix[4]arene (**3**) were prepared by changing the rotation speed of the spin-coating processes and the concentration of the solutions. While the sensor response of **3** linearly increased less than 15 µg upon the exposure to 2000-ppm of toluene vapor, the QCMs coated with **3** above 15 µg showed an unstable oscillation under the same voltage. In contrast, the QCMs with **1**-capped nanoparticles exhibited a linear increase when increasing the amount of sensing films until 40 µg. In a QCM resonator, the acoustic wave propagates through the bulk of the quartz crystal in a direction perpendicular to the surface. In the case of nanoparticle films, the generated wave from the surface of QCM can propagate within the sensing film and the

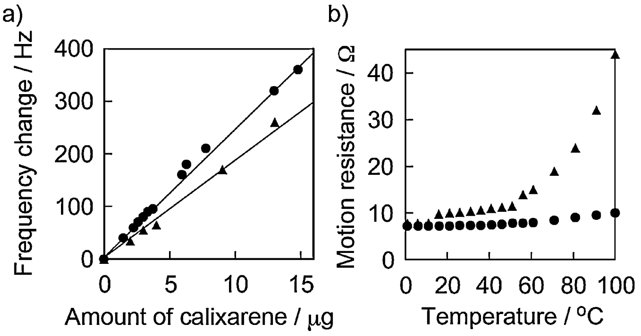

Figure 3. a) Dependence of calixarene amounts on sensor responses of QCM sensors coated with **1**-capped Au nanoparticles (●) and **3** (▲) upon exposure to 2000 ppm toluene vapor. The amounts of calixarene in the **1**-capped Au nanoparticles are estimated from the results of a TGA analysis. b) Motion resistance as function of operating temperature of QCMs coated with **1**-capped Au nanoparticles (●) and **3** (▲) measured using impedance analyzer.

adsorption of VOCs in the sensing films can be sensed as the frequency changes without any acoustic losses. On the other hand, the wave propagation within the film of **3** without Au nanoparticles is diminished by the viscoelastic characteristics of the films.

Figure 3a shows the sensor responses of QCMs coated with **1**-capped nanoparticles and **3** upon exposure to 2000 ppm toluene vapor. Although both films contain the same amount of calixarenes, the QCM with **1**-capped nanoparticles exhibited a larger sensor response than **3**. This large response can be attributed to a porous structure composed of Au nanoparticles owing to the high surface area. Calixarenes bound to the surface of Au nanoparticles work as the sensing sites within the porous films. The electrical characteristics of the QCMs coated with nanoparticle films were investigated using a network impedance analyzer. Figure 3b shows the temperature dependence of the motional resistance in the Butterworth–van Dyke equivalent circuit for the QCMs coated with thin films of **1**-capped nanoparticles and **3**.[21] The motional resistance provides information on the packing density and viscoelasticity of the films on a QCM. The motion resistances of the QCM with **1**-capped nanoparticles remained unaltered in the range of 0–100 °C, whereas the **3**-coated QCM showed a steep increase in motion resistance above 50 °C. Since the thermal structural changes of the organic segments in the nanoparticle films are limited in the interparticle space, the nanoparticle films can maintain a stable state.

In summary, Au nanoparticles capped with calixarene ligands are synthesized using the direct synthesis approach and are applied to the sensing films for VOCs. Nanoparticles capped with calixarene ligands exhibit a higher response for aromatic toluene compared to nanoparticles with monomeric ligands. The sensitivity for toluene is due to the interaction of aromatic vapor with a π-electron-rich calixarene cavity. Furthermore, the attachment of ligands to the surface of nanoparticles has two advantages for VOC sensing. One is the enhancement of the sensor response when using sensing films with large film thicknesses through the good resonance propagation of the nanoparticle films and limited swelling during VOC sorption. The other is the creation of porous structures by packing of nanoparticles. The calixarenes on the surface of nanoparticles work as high response sensing layers, and the interspace among the nanoparticles provides penetration pathways into the depth of the sensing film. Future experiments will focus on exploring the sensing ligands on Au nanoparticles to obtain a different response patterns and on investigating the selective response of VOC sensors in mixed VOCs.

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