

Supporting Information Available

Nano-assembled thin film gas sensor. III. Sensitive detection of amine odors using TiO₂/polyacrylic acid ultrathin film QCM sensors

Seung-Woo Lee,^{a,*} Naoki Takahara,^a Sergiy Korposh,^a Do-Hyeon Yang,^a
Kiyoshi Toko,^b and Toyoki Kunitake^a

^a*Graduate School of Environmental Engineering, The University of Kitakyushu, 1-1
Hibikino, Kitakyushu 808-0135, Japan*

^b*Graduate School of Information Science and Electrical Engineering, Kyushu
University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan*

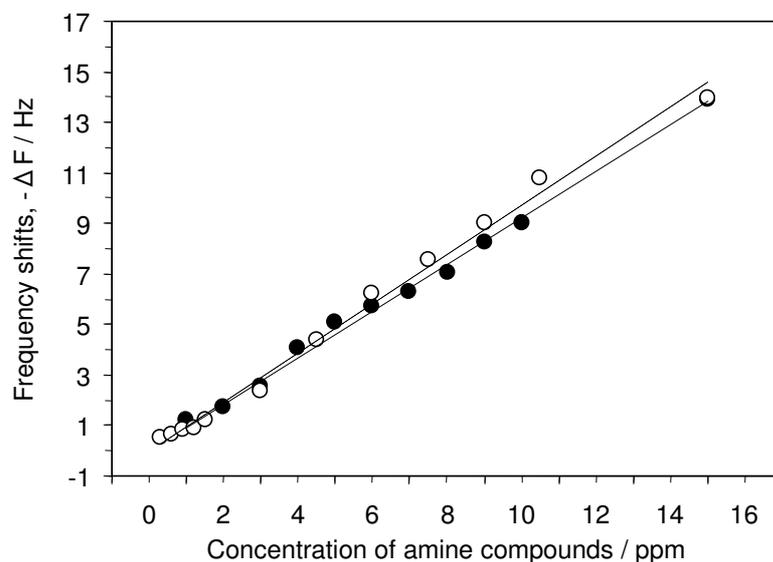


Figure S1: Correlation between generated ammonia gas (●) and standard ammonia gas in cylinder (○) for the sensor response on a GSSG (TiO₂/PAA)₂₀ film.

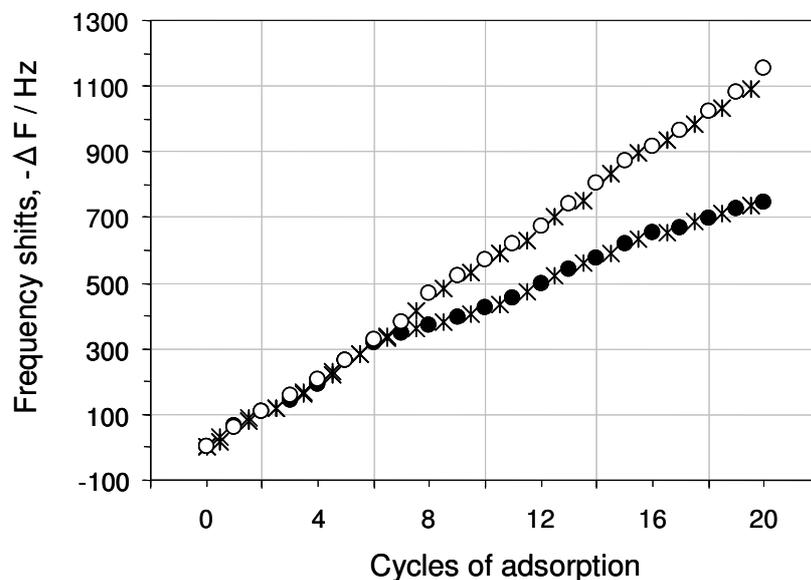


Figure S2. QCM frequency shifts during the alternate deposition of $\text{Ti}(\text{O}-n\text{Bu})_4$ and PAA on a gold-coated QCM resonator. (*) $\text{Ti}(\text{O}-n\text{Bu})_4$; (●) PAA_{25} and (○) PAA_{400} , respectively.

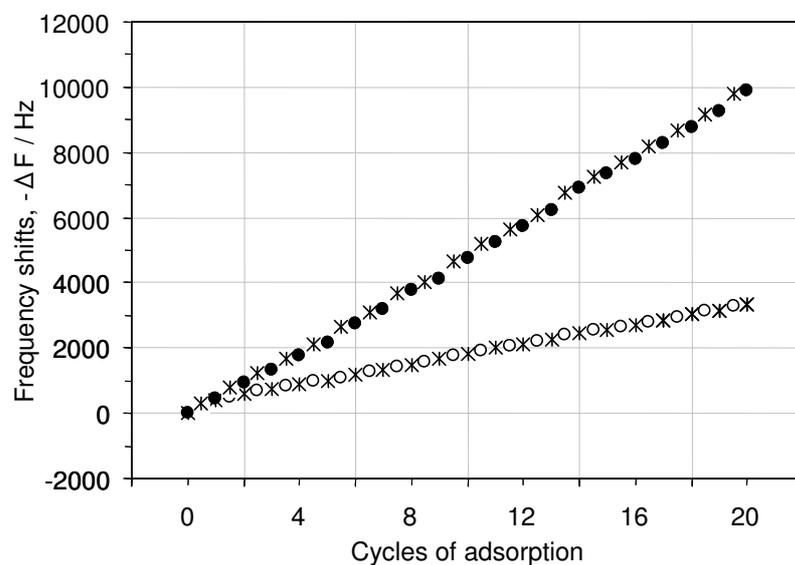


Figure S3: QCM frequency shifts during dip-coating deposition of $\text{TiO}_2/\text{PAA}_{400}$ bilayers on a gold-coated QCM resonator. (*) PAA; (○) 1 mM TiO_2 in toluene/ethanol ($v/v=1:1$) and (●) 10 mM TiO_2 in toluene/ethanol ($v/v=1:1$), respectively.

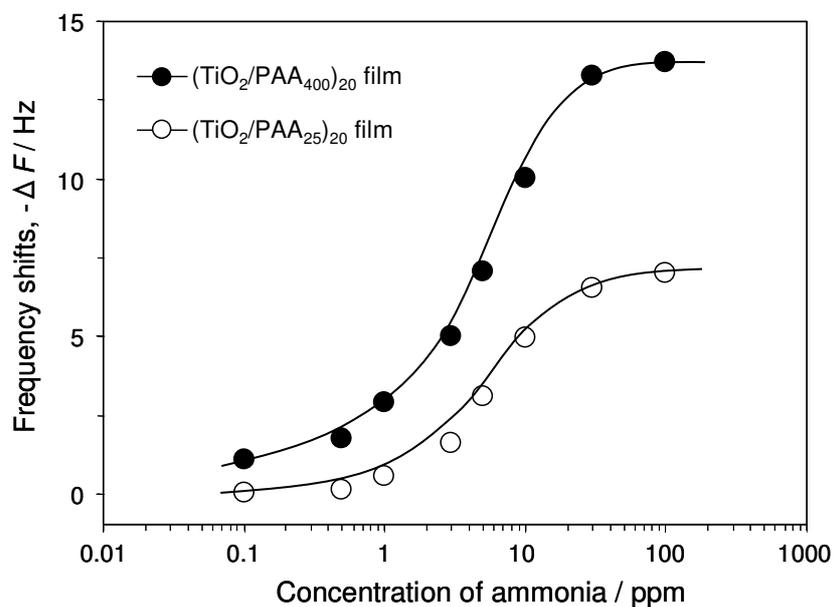


Figure S4. Comparison of the sensor response of GSSG $(\text{TiO}_2/\text{PAA})_{20}$ films exposed to ammonia for 20 sec: (●) $(\text{TiO}_2/\text{PAA}_{400})_{20}$ and (○) $(\text{TiO}_2/\text{PAA}_{25})_{20}$, respectively.

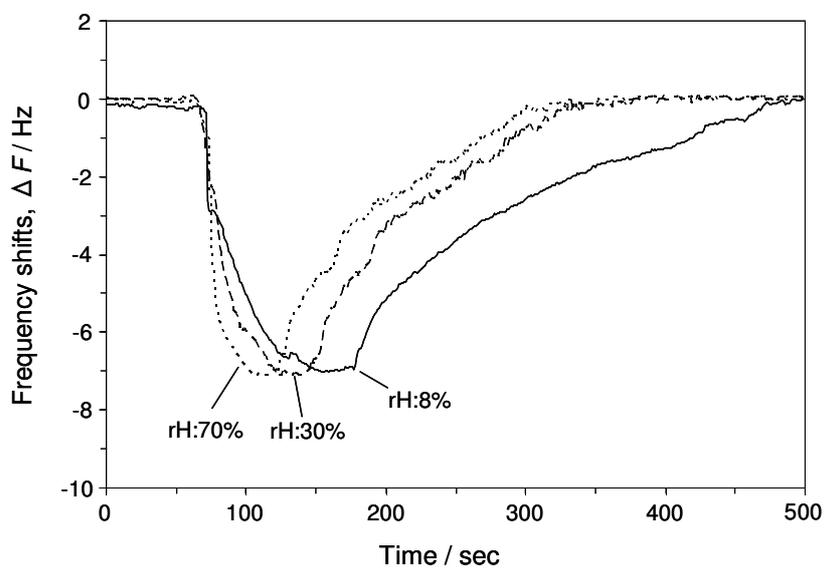


Figure S5: Comparison of the dynamic responses of the $(\text{TiO}_2/\text{PAA}_{400})_{20}$ to 6 ppm of ammonia at different relative humidities; rH=8%; rH=30% and rH=70%, respectively.

FT-IR measurements. A TiO₂/PAA bilayer film was assembled on a KBr pellet for FT-IR measurements. First, a TiO₂ gel layer was prepared by spin-coating (1 min, 3000 rpm): a 10 μ L solution of 100 mM Ti(O-ⁿBu)₄ in toluene/ethanol (1/1, v/v) was placed on the KBr pellet. Then, a 0.05 wt% PAA₄₀₀ solution in water was also deposited by spin-coating (1 min, 3000 rpm) and dried with N₂ gas. Infrared spectra were obtained using an FT-IR spectrometer spectrum 100 (PerkinElmer). All data were collected at a spectral resolution of 1 cm⁻¹.

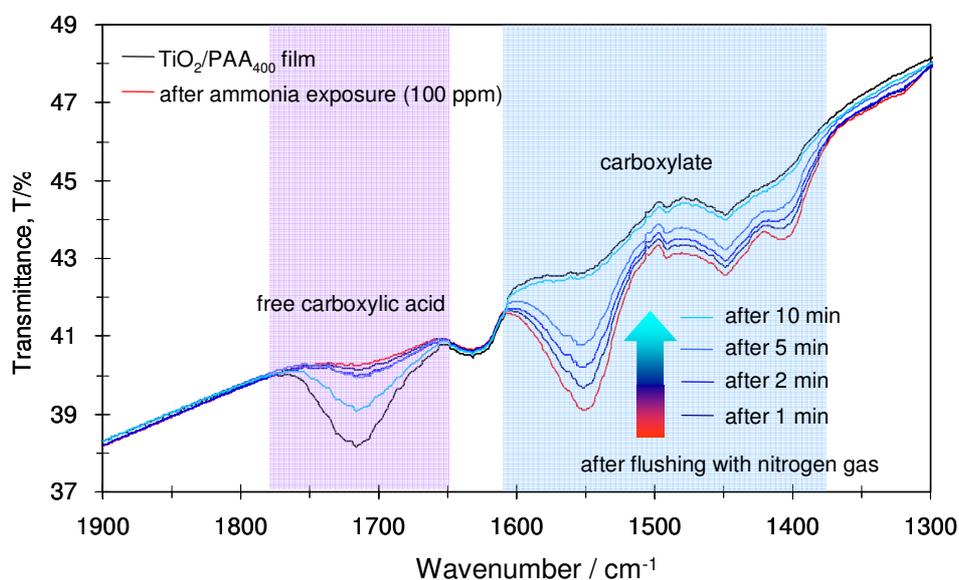


Figure S6: FT-IR spectral changes of a TiO₂/PAA film deposited on a KBr pellet before and after exposure to 100 ppm of ammonia.

Detailed experimental section

TiO₂/PAA Alternate Films. A gas-phase surface sol-gel (GSSG) process was used for the deposition of the (TiO₂/PAA)_n (n = 5, 10, and 20) films on a gold-coated quartz crystal microbalance (QCM) electrode, as described in our previous reports [24, 25]. Prior to the film deposition the gold-coated QCM electrode was treated with piranha solution (96.0% sulfuric acid/30.0-35.5% hydrogen peroxide, 3/1, v/v), rinsed with deionized water, and dried by N₂ gas. The cleaned gold-coated QCM electrode was hydroxylated by immersion in 10 mM 2-mercaptoethanol in ethanol for 12 h, rinsed with deionized water, and then dried with N₂ gas.

The PAA/TiO₂ film was deposited on the hydroxyl terminated QCM electrode, as shown in Figure 1. For the deposition of TiO₂ films, Ti(O-ⁿBu)₄ as metal alkoxide precursor was heated in a sealed flask at 85 °C and Ti(O-ⁿBu)₄ vapor was transferred by N₂ carrier gas into the deposition zone at a flow rate of 3L/min for 10 min. This was followed by flushing with N₂ gas, rinsing in deionized water and drying in N₂ flow, in order to remove the physisorbed alkoxide. The frequency change was measured after individual deposition. Subsequently, a QCM electrode coated with TiO₂ thin layer was immersed in aqueous solutions of 0.05 wt% of PAA₄₀₀ or 0.1 wt% of PAA₂₅ for 20 min at 25 °C. After each immersion the QCM electrodes were rinsed with deionized water,

followed by drying with N₂ gas. Consequently, alternate films of 5, 10 and 20 cycles (one cycle is a TiO₂/PAA bilayer) were prepared by alternate adsorption of Ti(O-ⁿBu)₄ and PAA on the QCM electrode with intermediate water washing for the hydrolysis of the metal alkoxide precursor, rinsing with deionized water, and drying by flushing with N₂ gas.

Pure TiO₂ Films. In order to study the response of pure TiO₂ films to amine odors as reference, the gas-phase sol-gel process was used for the deposition of pure TiO₂ films of 5, 10 and 20 cycles without adsorption of PAA.

Dip-Coated TiO₂ and TiO₂/PAA Alternate Films. The dip-coating method was employed to study the effect of the film thickness on the sensor parameter and thicker films of about 50–180 nm were fabricated. The substrate was immersed into a sol-solution and was withdrawn slowly with a given velocity to obtain a uniform coating-layer. The thickness of the deposited layer depended on the solution viscosity and velocities at which substrate is dipped and withdrawn from solution.

A mercaptoethanol-modified QCM electrode was immersed at 6.0×10^{-4} m/s into a solution of Ti(O-ⁿBu)₄ in toluene/ethanol (1, 5, and 10 mM, v/v = 1:1) and withdrawn at 1.6×10^{-4} m/s under the nitrogen atmosphere in order to fabricate a thick TiO₂ film. For the alternate deposition of TiO₂ and PAA, the QCM electrode was immersed into a 0.5

wt% aqueous solution of PAA₄₀₀ for 20 min at 25 °C, as described earlier in the section of **TiO₂/PAA Alternate Films**.

QCM Measurements. A quartz crystal microbalance (QCM, 9 MHz) device manufactured by USI System, Fukuoka, Japan, was used for monitoring film assembly and for the measurement of the amine-induced frequency change. The mass increase due to adsorption can be estimated from the QCM frequency shift by using a Sauerbrey's equation [23]. The following relationship is obtained between adsorbed mass, M (g), and frequency shift, ΔF (Hz), by taking into account the characteristics of used quartz resonators:

$$\Delta F \text{ (Hz)} = -1.832 \times 10^{-8} M / A \quad (1)$$

, where A is the surface area of the resonator (0.159 cm²). In the system employed for this work, a frequency decrease of 1 Hz corresponds to a mass increase of ca. 0.9 ng.

Gas Preparation. Desired gas concentrations are produced using a two-arm flow system, as shown in Figure 2. Compressed air was passed through a sample bottle containing an analyte to be measured in order to create an atmosphere saturated with analyte. The concentration z in the headspace of the bottle was calculated from the weight difference before (W_0) and after (W_1) flowing the compressed dry or humidified air through the bottle for 10 min at a flow rate of 1 L/min (giving a volume, $V = 10$ L).

A second air line bypassed the bottle, and the two were finally recombined with the final analyte concentration (volume fraction) c in the measurement chamber being calculated using:

$$c = \frac{L_1 \cdot z}{L_1(1+z) + L_2} \quad (2)$$

, where z is the mole fraction of the analyte in the headspace (i.e. the ratio of the partial pressure of the solution $p_s = (W_0 - W_1)/V$ at a given temperature to the atmospheric pressure P , i.e. $z = p_s/P$), and L_1 and L_2 are the flow rates of the air that passed and bypassed through the bottle, respectively.

L_1 was kept constant at 1 L/min and the analyte concentration was adjusted by varying L_2 . The baseline of each experiment was recorded by flowing dry air through the QCM chamber until the frequency reached equilibrium. Gas concentrations of the analytes (ammonia, *n*-butylamine, pyridine, ethanol, toluene and chloroform) were adjusted from 0 to 100 parts per million (ppm). In the case of ammonia gas, the gas concentration generated using this system was in good agreement with that of the standard ammonia gas in cylinder (see Figure S1).