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Nanoassembled Thin Film Gas Sensors. III. Sensitive Detection of Amine Odors Using TiO_2/Poly(acrylic acid) Ultrathin Film Quartz Crystal Microbalance Sensors

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Quartz crystal microbalance (QCM) gas sensors based on the alternate adsorption of TiO_2 and polyacrilic acid (PAA) were developed for the sensitive detection of amine odors. Individual TiO_2 gel layers could be regularly assembled with a thickness of ~0.3 nm by the gas-phase surface sol−gel process (GSSG). The thickness of the poly(acrylic acid) (PAA) layer is dependent on its molecular weight, showing different thicknesses of ~0.4 nm for PAA_{25} (Mw 250 000) and 0.6−0.8 nm for PAA_{400} (Mw 4 000 000). The QCM sensors showed a linear response to ammonia in the concentration range 0.3−15 ppm, depending on the deposition cycle of the alternate TiO_2/PAA layer. The ammonia binding is based on the acid−base interaction to the free carboxylic acid groups of PAA and the limit of detection (LOD) of the 20-cycle TiO_2/PAA_{400} film was estimated to be 0.1 ppm when exposed to ammonia. The sensor response was very fast and stable in a wide relative humidity (rH) range of 30−70%, showing almost the same frequency changes at a given concentration of ammonia. Sensitivity to *n*-butylamine and ammonia was higher than to pyridine, which is owing to the difference of molecular weight and basicity of the amine analytes. The alternate TiO_2/PAA_{400} films have a highly effective ability to capture amine odors, and the ambient ammonia concentration of 15 ppm could be condensed up to ~20 000 ppm inside the films.

Detection of odorous amine compounds is a target of primer importance in many areas of human activities.[1,2] Amine compounds, especially, have been used as an indicator of the food quality[3] and are also a challenging target of environment pollutant detection.[4] Among others, ammonia could be regarded as a “biomarker” for the diagnosis of several diseases and therefore the device for the ammonia measurement with the detection limit of 50−2000 ppb and fast response time are highly desired.[1]

Recently, organic polymers were deposited on different transducers as the sensitive element for the ammonia detection,[5] such as potentiometric,[6] optical,[7] and mass sensitive ones.[8] Among these techniques, quartz crystal microbalance (QCM) is extremely sensitive and a powerful tool for monitoring mass changes in the nanogram range.[9,10] The basic principle of QCM sensors is the measurement of the frequency shift as a result of the mass adsorbed on the QCM resonator. How to modify the resonator surface properties becomes an essential issue for enhancing the range of applications of the QCM sensor, and deposition of thin films on the QCM resonator surface allows sensitive and selective determination of particular chemical analytes to be achieved.[11−13] The layer-by-layer (LbL) process is a versatile technique for the deposition of multilayered nanothin films onto different substrates.[14,15] Recently, we have employed the LbL process for the preparation of multilayered organic films as sensitive

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