Supporting Information for

Trimethylamine sensor based on zinc hydroxystannate cubes for long-term evaluating the freshness of four types of seafood

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1. Chemicals and Materials

All reagents， including zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) and sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$), were analytic grade from Aladdin Reagent (China) Co., Ltd. and used as received without further purification. All the chemical reagents were directly used as obtained from commercial sources without further purification.

2. Synthesis of $ZnSn(OH)_6$ cubes

In a typical experiment, 10 mmol of $ZnSO_4 \cdot 7H_2O$ was added into 100 mL of deionized water, and the solution was stirred at room temperature until $ZnSO_4 \cdot 7H_2O$ was dissolved completely. Then an appropriate $Na_2SnO_3 \cdot 3H_2O$ solution was dropped into $ZnSO_4 \cdot 7H_2O$ solution, making the molar ratio of [Zn]/[Sn]=1:1. After the completion the above steps, the mixed solution was under continuous magnetic stirring for 5 h. After the reaction, the precipitates were collected by centrifugation, washed with DW for several times to remove residual ions in the products. The final products were then dried in air at 100 ℃ for 8 h before characterization.

3. Characterization

Powder X-ray diffraction data were obtained on a Panalytical X'Pert'3 Powder advance diffractometer with a graphite-monochromatized Cu Ka radiation. The surface morphologies of the materials were observed by Zeiss Sigma300 scanning electron microscope (SEM). For the characterization of the functional groups, we employed Fourier-transform infrared spectroscope (FTIR, Thermo Scientific Nicolet iS20,

Thermo Fisher Scientific).

4. Fabrication and Test Methods of the QCM Sensor

To ensure sensor consistency, we employed the widely used drop-coating technique in the QCM sensor manufacturing field to deposit the as-prepared 20 mg/mL $ZnSn(OH)_6$ cubes dispersion onto the silver surface of the QCM chips by a micropipette. In order to evaluate the effect of the depositing amount of $ZnSn(OH)_6$ cubes on sensor performance, the sensors with 1, 2, 3, and 4 μL of $ZnSn(OH)_6$ cubes deposited on the electrode of QCMs were fabricated. The corresponding sensors were labeled as QCM-1, QCM-2, QCM-3, and QCM-4. The absolute ethanol dispersion of the synthesized materials after ultrasonic processing was drop-casted onto QCM surface, and the as-fabricated sensor was dried in an infrared box for evaporating of ethanol. According to Sauerbrey equation ($\Delta F = -2.2\times10^{-6} f^2 \Delta m/ A$), the frequency shift of QCM resonator (ΔF) is proportionate with the increased mass on silver electrode (Δm) [1]. As shown in Figure S1, QCM chip was vertically suspended inside a sealed chamber with gas inlet/outlet. The air (15 sccm) generated by an air generator was used as the carrier gas. Because the evaporation point of trimethylamine is relatively high, a heater is indispensable. All tests were conducted at ambient temperature and relative humidity (RH) of 50%. Two running fans can accelerate the dispersion of gaseous trimethylamine homogeneously. As a typical process, QCM sensor was flushed with air until a steady fundamental frequency was obtained. Then, the liquid trimethylamine analyte with calculated volume was introduced to the chamber by a microliter syringe. The exact volume of the injected trimethylamine analyte liquid was concretely

calculated in μl based on the following equation: $Vl=cVM10^{-6}/22.4dp$, where Vl represents the volume of liquid in μl, c is the liquid concentration in ppm, M represents the molecular weight, d is the liquid density, and p represents the degree of purity. Then, following the sensing test, a frequency shift to analyte would be obtained after a period of time. The frequency shift was living measured by a digital controller and recorded by a desk top computer. At the end of each testing cycle, continuous air would wash away the analyte to re-establish the fundamental frequency.

5. Real sample measurement

Four kinds of seafood, including ribbonfish, squid, prawn, and swimming crab, were purchased at Fengchuan Farmers' Market (Hangzhou, China). The preparation process of the seafood samples was as follows: Firstly, each of the four kinds of seafood was divided into 11 samples respectively, with each sample weighing 20 g, and they were placed in a refrigerator at 4 °C from the first day to the eleventh day. Secondly, the 11 samples were put into headspace bottles with a volume of 1.158 liters respectively. Finally, a 50 ml syringe was used to absorb and inject the volatile gas, and the designed QCM sensor was used to conduct repeated tests for 11 days, with one test per day, in order to detect the changes in the freshness of the seafood and determine the TMA content of the seafood. As a control experiment, each of the four kinds of seafood was divided into 5 samples respectively, with each sample weighing 20 grams, and they were placed in a room temperature environment of 25 °C from the first day to the fourth day. Then, the 5 samples were put into headspace bottles with a volume of 1.158 liters respectively. Finally, a 50 ml syringe was used to absorb and inject the volatile gas, and

the designed QCM sensor was used to conduct repeated tests for 3 days, with one test every half day, in order to detect the changes in the freshness of the seafood and determine the TMA content of the seafood.

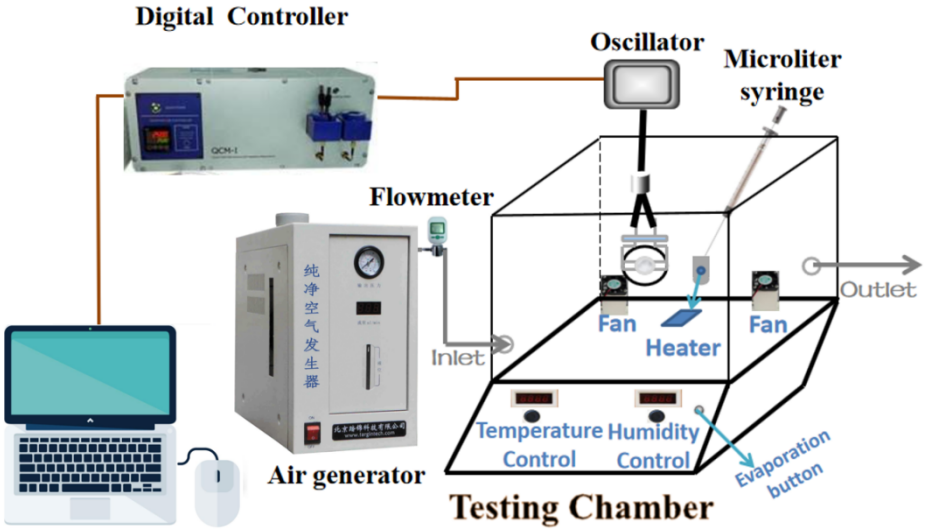

Figure S1. Schematic of the sensing testing system.

References

1. L. Wang, Z. Wang, Q. Xiang, Y. Chen, Z. Duan and J. Xu, *Sensors and Actuators B: Chemical*, 2017, **248**, 820-828.