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Selectivity of a QCM gas sensor modified by ZnSn(OH)$_6$ *via* analysis of adsorption thermodynamics and kinetics

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In this paper, a novel analysis approach was employed to achieve the selectivity of a quartz crystal microbalance (QCM) sensor. A QCM sensor chip modified by ZnSn(OH)$_6$ (ZSH) was used to identify gases (CO, CH$_4$ and O$_2$) with different volume fractions. The combination of adsorption thermodynamics and adsorption kinetics was firstly used to identify gas species. The relationship between the adsorption thermodynamic parameter (adsorbed mass amount in molar) and the adsorption dynamic parameter (adsorption rate constant, k) was used to characterize the selectivity and concentration of gases. It showed that the method is useful but it still has some limitations. Another approach was also proposed. The kinetic parameter t_{90} and thermodynamic parameter Δm were employed as characteristic parameters to determine the species and concentration of a gas. The results showed that three kinds of gas with different volume fractions were located in different regions of the t_{90}-Δm two-dimensional graph. We can identify single gases with different volume fractions by enriching the t_{90}-Δm graph with additional data. It is believed that this new analysis method would be promising in gas species identification with QCM sensors.

Introduction

Gas sensors have attracted considerable research interest due to their latent applications in many fields, including environmental monitoring, medical diagnosis, public security, agriculture and food production. Although many techniques and methods have been used in gas sensors, it is still urgent to develop new gas sensors with the functions of reliability, small size, low-cost, and system portability.[1–3]

In recent years, quartz crystal microbalances (QCMs) have been widely used as gas sensors due to their ultra-high sensitivity in mass variation in the nano-gram level. N. V. Quy[4] reported enhanced NH$_3$ gas sensing properties of a QCM sensor by increasing the length of vertically orientated ZnO nanorods. I. E. Tothill[5] developed an immune-sensor for the detection of the food pathogen campylobacter jejuni by a QCM. S. Öztürk[6] showed that Pd-doped ZnO nanorods have been synthesized as QCM sensors of volatile organic compounds (VOCs) at room temperature. J. He[7] studied graphene oxide as QCM sensing layers for the detection of formaldehyde and so on.

Although QCMs are powerful in recording frequency and mass variations, it is still hard to distinguish in detail the species of adsorbed gas, which always hampers the development and application of this technique. Generally, QCM sensors with a modified surface exhibit high sensitivity to one or several kinds of gas. However, selectivity is the disadvantage of QCM sensors. Most of the previous research studies discussed typical gas sensing based on the adsorption quantity (commonly frequency variation, ΔF, or adsorbed mass, Δm). The maximum variations of frequency or adsorbed mass were commonly used as a characteristic parameter to explain the adsorption behaviour. In addition, recording the adsorption of gas on a QCM sensor can lead to a dynamic adsorption process and be interpreted as a thermodynamic parameter, which is far from our expectation for the identification of gas species and concentration determination. In fact, the adsorption behaviour of various gases based on QCMs typically involves both adsorption thermodynamics and adsorption kinetics. Different kinds of gas molecule should exhibit different adsorption kinetics, even in the same molar concentration. The combination of adsorption thermodynamics and kinetics would thus be an important way of identifying unknown gases.

To the best of our knowledge, there are no published papers about the combination of adsorption thermodynamics and kinetics of QCM sensors to identify species and concentrations of gases. Herein, a QCM chip modified by zinc hydroxystannate (ZnSn(OH)$_6$, ZSH)[8–10] was used to measure three kinds of gas (CO, CH$_4$ and O$_2$). Based on our preliminary research, the QCM

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sensor coated with ZSH was found to exhibit good sensitivity properties to single gases, such as CO and CH_4.[11,12] However, when the QCM chip was exposed to a mixture of gases, it was hard to identify the type and concentration of a gas. Therefore, in this paper, the reason why ZSH was chosen to modify QCM chips as gas sensors was that a new analysis approach would be utilized to distinguish the species of gas compared with conventional methods based on the same sensing materials. Adsorption thermodynamics and kinetics were analysed simultaneously using new methods in order to achieve QCM sensor selectivity.

Results and discussion

The crystal structures and morphologies of the as-obtained samples were investigated by XRD and SEM, respectively. Fig. 1(a) shows that all peaks perfectly coincided with those of standard ZSH with a perovskite structure (JCPDS no. 20-1455), affirming that the as-synthesized sample has a typical face-centered cubic crystal structure. The sharp and strong intensity of the diffraction peaks of ZSH imply that the phase of ZSH is well crystallized. The morphology of the sample in Fig. 1(b) characterized by SEM shows that a large number of cubic crystals with side lengths of approximately 202 nm were uniformly distributed on the surface of the substrate. Meanwhile, some nanopores were found on the surface of the cubic ZSH, which are beneficial for gas adsorption.[11,12]

Fig. 2 shows the response of the ZSH film modified QCM sensor in different concentrations of CO, CH_4 and O_2. The data are presented as the mass variation *versus* time. The QCM sensor is very sensitive to the three tested gases. It is obvious that the adsorbed mass rises with an increase of all the gas volume fractions. The processes of adsorption and desorption exhibit good reversibility, which indicates that ZSH is a promising material for the detection of gases. Meanwhile, this also demonstrates that the adsorbed mass presents significant differences for typical gases (CO, CH_4 and O_2) at the same concentration. Specifically, CO displays a superior adsorption ability to other gases while the smallest adsorbed mass was observed when exposed to O_2.

In most of the previous research studies, data similar to that shown above had been presented to characterize the adsorption of the gas sensor, from which only limited information can be acquired. In particular it is very hard to distinguish the gas species, or to characterize the selectivity. It is well known that the adsorption rate and the equilibrium adsorption amount are determined by both typical gas molecules and sensor materials. Therefore, we can identify the gas species by establishing adsorption kinetics and thermodynamic characteristic parameters.

More detailed information can be obtained from further data analysis of adsorption processes. The adsorption process of the three gases on the sensor follows a second-order model.[13–15] As for the adsorption process, if it obeys a second-order adsorption model, it commonly conforms to the following equation:

$$\frac{t}{Q_t} = \frac{1}{k}Q_{e,cal}{}^2 + \frac{1}{Q_{e,cal}}t \tag{1}$$

where $Q_{e,cal}$ is the equilibrium adsorption amount taken from calculations and k is the adsorption rate constant. Fig. 3(a) presents the $\frac{t}{Q_t} \sim t$ relationship of 3% O_2, in which the plot shows good linearity. It demonstrates that the adsorption process of 3% O_2 on the sensor surface is a second-order adsorption. Hence, the intercept and slope in the plot shown in Fig. 3(a) can be obtained from the following equations:

$$Q_{e,cal} = \frac{1}{a} \tag{2}$$

$$k = \frac{1}{b}Q_{e,cal}{}^2 \tag{3}$$

where a and b are the slope and intercept of the fitting equation, respectively. k (ng cm^{-2} s^{-1}) represents the adsorption rate constant of a gas at the sensor surface. The bigger the k value, the faster the adsorption rate.

Herein, the relationship between the adsorption thermodynamic parameter (adsorbed mass amount in molar) and the adsorption dynamic parameter (adsorption rate constant, k) has been used to try to characterize the selectivity. Fig. 3(b) presents the behaviour of k and the adsorbed mass amount in molar of
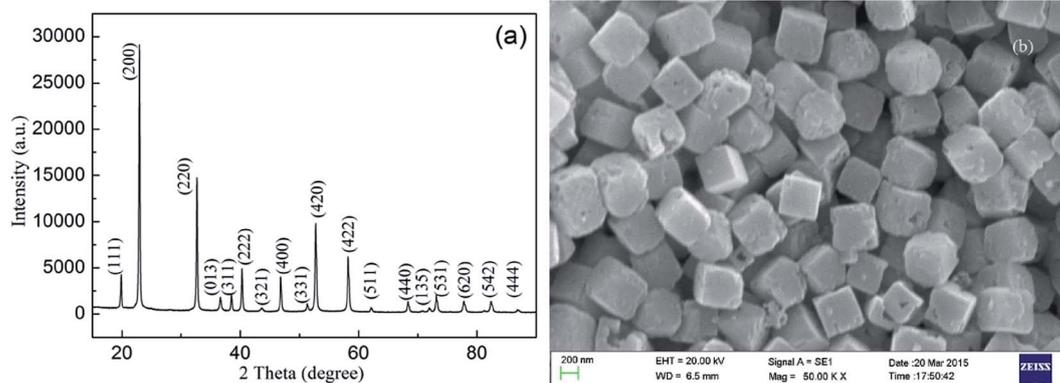

Fig. 1   (a) XRD pattern of the sample, matching that of standard ZSH (JCPDS 20-1455). (b) Typical SEM image of the synthesized ZSH.
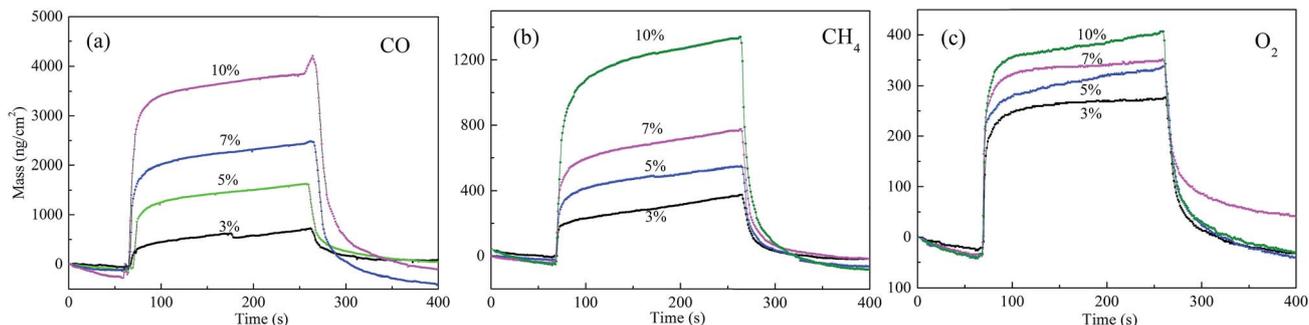
Fig. 2 Response and recovery curves of the QCM sensor to different gases with different volume fractions.

the three tested gases with different concentrations. All the dots in the figure corresponding to a specific gas are linear. The plot also reveals that a gas with specific characteristics and concentration can be located at a certain position of the plane coordinates, such that different gases are located at different zones of the figure. CO varies from the bottom left corner to the top right corner of the figure, CH_4 just stands right behind CO, and O_2 is located at the bottom left corner of the figure. As for an unknown gas which should, of course, be one of the three gases, it is possible to characterize its concentration and type by inputting the analysed data into the plane coordinates. However, the method still has its limitations. As we can see from Fig. 3(b), CO and O_2 are almost along the same line. If we widened the range of the concentration, the data might then overlap. Moreover, the data of CH_4 and CO were very close at low concentrations.

Hence, another new analysis method has also been proposed, which is based on characteristic parameters of adsorption thermodynamics and kinetics as well. t_{90}-Δm of various gases, in which t_{90} refers to the time taken to reach 90% of the maximum adsorption amount and Δm is the maximum adsorption amount, has been utilized innovatively for the identification of unknown gases as shown in Fig. 4.

The kinetics of the gas adsorption process are based on the fitting of mass–time curves. Fig. 4(a) shows the adsorbed mass (Q_t)–time curves and the exponential fitting results. The exponential fitting used in the figure corresponds to the following equation:

$$Q_t = Q_{e,exp} + A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \qquad (4)$$

where Q_t is the adsorbed mass at time t, $Q_{e,exp}$ is the equilibrium adsorption amount obtained from the fitting of experimental data, A_1 and A_2 are pre-exponential factors, k_1 and k_2 are adsorption factors and t is time. The fitted $Q_{e,exp}$ represents the maximum adsorbed mass at the sensor surface. t_{90} can be obtained from the fitted data, as is shown in Fig. 4(a).

t_{90}-Δm is a competitive method to combine kinetic and thermodynamic processes, as is shown in Fig. 4(b). It can be seen that CO/CH_4/O_2 with different volume fractions are located in different regions in the t_{90}-Δm two-dimensional graph. Hence, we can identify single gases with different volume fractions by enriching the t_{90}-Δm map *via* measurements of more kinds of gas to get a t_{90}-Δm database. This new analysis method can achieve the selectivity of QCM sensors.

Experimental

In a typical synthesis procedure, 1 mmol of analytical grade zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was dissolved into 40 mL of deionized water until $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved completely by stirring at room temperature (25 °C). Then 1 mmol $SnCl_4 \cdot 5H_2O$ was added into the $Zn(CH_3COO)_2 \cdot 2H_2O$ solution. Lastly, sodium hydroxide (NaOH) was added to the above mixture solution under magnetic stirring for 30 min. The homogeneous solution was quickly transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL, it was
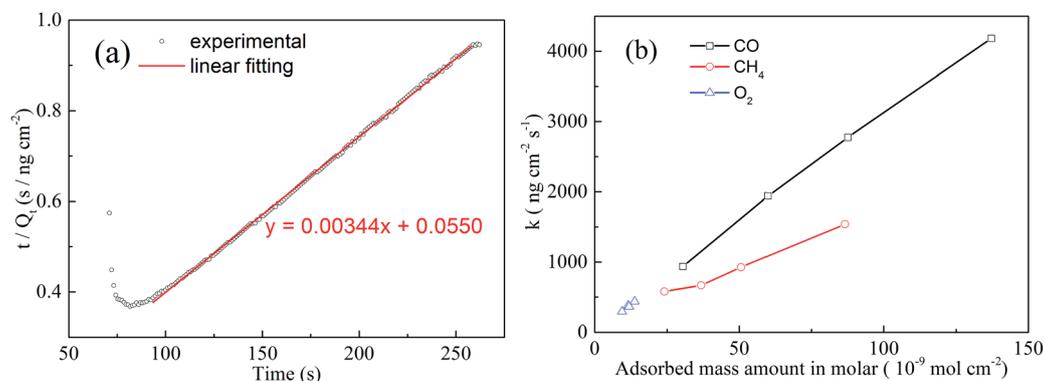

Fig. 3 (a) Fitting of the adsorption process by a second-order equation of 3% O_2. (b) Plane coordinates to interpret the gas type and concentration.
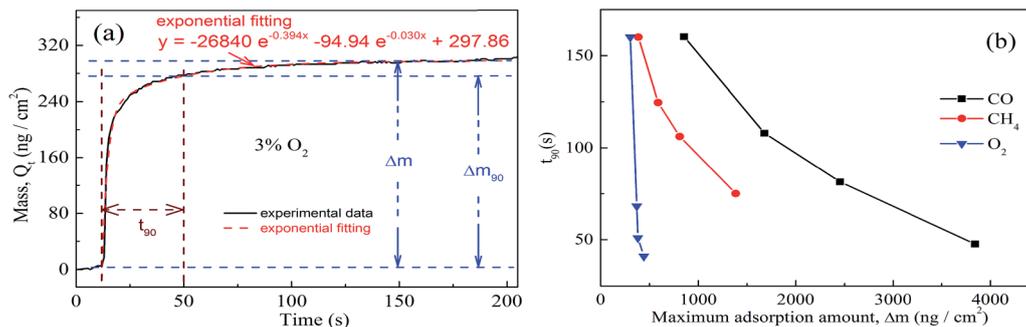
Fig. 4 (a) Exponential fitting of the adsorption process of 3% O_2. (b) t_{90}-Δm distribution of typical gases, in which t_{90} refers to the time taken to reach 90% of the maximum adsorption amount and Δm is the maximum adsorption amount.
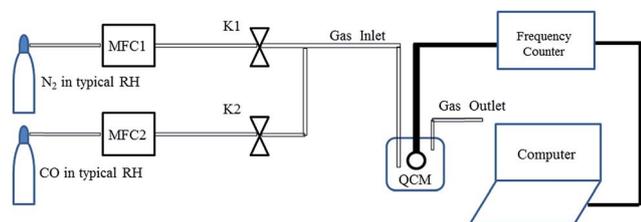

Fig. 5 The QCM measurement used during gas sensing tests.

heated at 80 °C for 20 h, and then cooled down naturally. The products were washed with absolute ethanol and double distilled water three times and kept in suspension conditions as final products for further characterization and gas sensing testing. X-ray powder diffraction (XRD, X'Pert PRO) using CuK$_\alpha$ radiation ($\lambda = 0.1548$ nm) was used for determining the phase purity and crystal structure of the product. The morphology was characterized by scanning electron microscopy (SEM, EVO MA15). The gas-sensing properties of ZSH were studied with a QCM sensor system at room temperature in dry conditions.

In detail, a ZSH-based CO sensor was prepared by the following steps: a gold-coated QCM was cleaned with ethanol for 20 min. Then the QCM was rinsed in deionized water and dried at room temperature in a dry nitrogen atmosphere. The suspension was dropped onto the QCM and the coating was dried in a furnace at 80 °C for 1 h. Fig. 5 shows a two channel flow system, which was used to detect QCM signals when exposed to volume fractions of typical gases (CO, CH$_4$ and O$_2$) at room temperature (25 °C) in dry conditions to study the adsorption and desorption processes. Two mass flow controller (MFC) valves were used to dilute the CO concentrations with N$_2$. The MFC system was used to change the ratio in the testing chamber to obtain the desired gas volume fraction.

Conclusions

In summary, a ZSH-modified QCM sensor was used for detecting different concentrations of CO, CH$_4$ and O$_2$. The following conclusions can be drawn:

(1) The ZSH-modified QCM sensor was very sensitive to different concentrations of CO, CH$_4$ and O$_2$. The adsorbed mass presented significant differences for gases at the same concentration. CO displayed a superior adsorption ability to other gases, while the sensor was least sensitive to O$_2$.

(2) The relationship between the adsorption thermodynamic parameter (adsorbed mass amount in molar) and the adsorption dynamic parameter (adsorption rate constant, k) can be used to characterize the selectivity and concentration of a gas. But it still has some limitations.

(3) The relationship of characteristic parameters, t_{90}-Δm, was useful to determine the species and concentrations of gases. This new analysis method would be promising in gas species identification with QCM sensors.

Conflicts of interest

We declare that there exists no conflict in the submission of this manuscript, and all the authors have seen the manuscript and approved submission to the journal. I would like to declare on behalf of my co-authors that the work described is original research that has not been published previously, and is not under consideration for publication elsewhere, in whole or in part.

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