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 $\Delta m$ 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 $t_{90}$-$\Delta m$ two-dimensional graph. We can identify single gases with different volume fractions by enriching the $t_{90}$-$\Delta m$ graph with additional data. It is believed that this new analysis method would be promising in gas species identification with QCM sensors.

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, $\Delta F$, or adsorbed mass, $\Delta m$). 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)$_6$) 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 selectivity. Adsorption thermodynamics and kinetics were analysed using 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.

Fig. 2 shows the response of the ZSH film modified QCM sensor in different concentrations of CO, CH4 and O2. 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, CH4 and O2) at the same concentration. Specifically, CO displays a superior adsorption ability to other gases while the smallest adsorbed mass was observed when exposed to O2.

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. As for the adsorption process, if it obeys a second-order adsorption model, it commonly conforms to the following equation:

\[
\frac{t}{Q_t} = \frac{1}{k} Q_{\text{cal}}^2 + \frac{1}{Q_{\text{cal}}} t
\]

where \(Q_{\text{cal}}\) is the equilibrium adsorption amount taken from calculations and \(k\) is the adsorption rate constant. Fig. 3(a) presents the \(t/Q_t\) versus \(t\) relationship of 3% O2, in which the plot shows good linearity. It demonstrates that the adsorption process of 3% O2 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:

\[
Q_{\text{cal}} = \frac{1}{a}
\]

\[
k = \frac{1}{b} Q_{\text{cal}}^2
\]

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

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**Fig. 1** (a) XRD pattern of the sample, matching that of standard ZSH (JCPDS 20-1455). (b) Typical SEM image of the synthesized ZSH.
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, CH4 just stands right behind CO, and O2 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 O2 are almost along the same line. If we widened the range of the concentration, the data might then overlap. Moreover, the data of CH4 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. $t_{90} \Delta m$ of various gases, in which $t_{90}$ refers to the time taken to reach 90% of the maximum adsorption amount and $\Delta m$ 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:

$$Q_t = Q_{e, exp} + A_1 e^{-k_1 t} + A_2 e^{-k_2 t}$$

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).

$t_{90} \Delta m$ is a competitive method to combine kinetic and thermodynamic processes, as is shown in Fig. 4(b). It can be seen that CO/CH4/O2 with different volume fractions are located in different regions in the $t_{90} \Delta m$ two-dimensional graph. Hence, we can identify single gases with different volume fractions by enriching the $t_{90} \Delta m$ map via measurements of more kinds of gas to get a $t_{90} \Delta m$ 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$_3$COO)$_2$$\cdot$2H$_2$O) was dissolved into 40 mL of deionized water until Zn(CH$_3$COO)$_2$$\cdot$2H$_2$O was dissolved completely by stirring at room temperature (25°C). Then 1 mmol SnCl$_4$$\cdot$5H$_2$O was added into the Zn(CH$_3$COO)$_2$$\cdot$2H$_2$O 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
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, XPert PRO) using CuKα radiation (λ = 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, CH₄ and O₂) 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 N₂. 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, CH₄ and O₂. The following conclusions can be drawn:

(1) The ZSH-modified QCM sensor was very sensitive to different concentrations of CO, CH₄ and O₂. 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 O₂.

(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, t₉₀Δm, 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.

Acknowledgements

This work was financially supported by the National Science Foundation of China (51641108).

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