FACILE FABRICATION OF ANILINE SENSOR BY USING COMMERCIAL CALCIUM SILICATE HYDRATE NANO SHEETS AS SENSING MATERIAL

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Various aniline sensing materials have excellent properties based on quartz crystal microbalance (QCM) transducer, but their synthesis processes are complex. Herein, commercial calcium silicate hydrate nanosheets (CSH-S) was utilized for facile fabrication of aniline sensor based on QCM platform. This sensor was capable of detecting 0.1 ppm aniline, and the response time (14 s) and recovery time (16 s) were short. Besides, the devices could restore sensitivity after 30 days, demonstrating excellent stability. In addition, variable temperature experiment combined with simulation calculation methods were carried out to study the adsorption of aniline on CSH-S surfaces, then the sensing mechanism was revealed. This work opens up a rapid and convenient method for detecting gaseous aniline.

Keywords: gas sensor; quartz crystal microbalance; aniline; calcium silicate hydrate.

INTRODUCTION

Aniline is one of the most important amine substances, mainly used in the manufacture of dyes, drugs, resins, and can also be used as a rubber vulcanization accelerator.¹ According to the list of carcinogens published by the World Health Organization’s International Agency for Research on Cancer, aniline is on the list of carcinogens.² Real-time sensing of gaseous aniline has recently attracted attention, especially for chemosensitized sensors. The current method used for detecting aniline is fluorescence sensing, which includes o-carborane modified pyromellitic diimide derivative, Eu@UiO-66(COOH), and others.³,⁴ Another widely used method is semiconductor sensing, such as ZnO-TiC, Ce doped ZnO, etc.¹,⁵

Based on quartz crystal microbalance (QCM), a low power mass-sensitive platform,⁶ several aniline sensing sensors have also emerged. The pristine QCM has some disadvantages, such as limited sensitivity, sensitivity to environmental interference, frequency drift, and mass loading effects. To optimize these issues, it is common practice to modify the QCM surface with sensing materials.⁷ The working principle of this type of sensors is mainly based on the mass change caused by the adsorption of target gas by the sensitizing material on the QCM surface, and the mass change is converted into a frequency change through the Sauerbrey equation, and then output as an electrical signal.⁸ The Sauerbrey equation is expressed as Equation 1.⁹

\[ \Delta F = \Delta \frac{m}{A} \times f^2 \times 2.2 \times 10^{-6} \times f^2 \times \Delta m/A \]  

where \( f \) is the basic resonance frequency, \( A \) is the working area of the electrode, the frequency shift (\( \Delta F \)) depends on the mass change (\( \Delta m \)). The QCM based sensitizing materials for detecting aniline are mainly concentrated in metal-organic frameworks (MOFs),¹⁰,¹¹ amino polymer materials,¹² etc. However, it is complex to synthesize the above materials in large quantities and ensure their quality. Therefore, it has broad market prospects and time saving significance to find some commercial materials and design them into high-performance aniline sensors facilely.

Carbide slag is the by-product of the hydrolysis of calcium carbide to produce acetylene, and its main component is calcium hydroxide, which is strongly alkaline.¹³ Currently, carbide slag is mainly used for flue gas treatment, CO₂ capture, or as a chemical additive.¹⁴ Recently, calcium silicate hydrate (CSH) nanomaterials can be developed using calcium carbide slag as a raw material for applications such as heavy metals recovery.¹⁵

Here, a calcium silicate hydrate nanosheets (CSH-S) acquired commercially has been utilized to facile fabrication of sensor aiming at detect gaseous aniline based on QCM platform, as shown in Figure 1. The sensing performance parameters of this sensor are excellent, including sensitivity, selectivity, stability, etc. The sensing mechanism between CSH-S and aniline was analyzed by means of variable temperature experiment and simulation calculation. This work provides a potential way for rapid design of aniline sensors.

EXPERIMENTAL

Materials and sensor fabrication process

A high-purity (99%) calcium silicate hydrate nanosheets (CSH-S)
The results of utilizing QCM as an aniline sensor in recent years have displayed the potential of this technique in environmental monitoring and other applications. To verify which group plays a key role in aniline detection, the interaction energies between aniline molecule and the multiple functional groups of sensing material were calculated according to the following Equation 3. The sensing material will be named $S$:

$$
\Delta H_{\text{aniline-S}}(\text{kJ mol}^{-1}) = H_{\text{aniline}}(\text{kJ mol}^{-1}) - H_{\text{aniline}(\text{kJ mol}^{-1})} - H_0(\text{kJ mol}^{-1})
$$

(Related Equation 3)

RESULTS AND DISCUSSION

Materials characterization

FTIR spectra of fresh CSH-S sample is presented in Figure 2. The CSH-S exhibited an obvious adsorption peak around 971 cm$^{-1}$, corresponding to the antisymmetric stretching vibration of Si–O–Si. Similarly, a bending vibration peak of Si–O–Si appeared around 458 cm$^{-1}$. The above two peaks demonstrated that the CSH-S possessed a Si–O tetrahedron structure. Besides, the CSH-S exhibited a peak of Ca–O around 1441 cm$^{-1}$. Furthermore, the CSH-S showed obvious vibration peaks at 1634 and 3457 cm$^{-1}$. These two peaks are reflections of hydroxyl groups, indicating that there were two linkage types of hydroxyl groups in CSH-S: Ca–OH and Si–OH.$^{17}$ The XRD pattern (Figure 2S, supplementary material) shows the low crystallinity of CSH-S sample. Besides, the consistency between the position of the characteristic peaks of CSH-S sample and the previous literature on CSH indicates the successful synthesis of calcium silicate hydrate.$^{15}$

Gas-sensing properties

The results of utilizing QCM as an aniline sensor in recent years are presented in Table 1. The table demonstrates that scientists have identified various MOFs and polymers, which were transformed into sensing materials. These materials were then coated onto QCM for aniline detecting. Here, commercial calcium silicate hydrate nanosheets was used to make sensing material selective to aniline vapor. Figure 4a depicts the dynamic frequency shift result of CSH-S.
coated QCM sensor when exposed to 0.1-2 ppm gaseous aniline. It can be observed that with the increase of gaseous aniline concentration gradient, the frequency shift of the prepared CSH-S coated QCM sensor shows an upward trend. The frequency shift to concentrations of 0.1, 0.25, 0.5, 1 and 2 ppm were −14.7, −27.4, −43.5, −76.3 and −132.2 Hz, respectively. The fitting function of the frequency shift (y) and aniline concentration (x) of the CSH-S coated QCM sensor is depicted in Figure 4b. The fitting function can be expressed as $y = -61.2x - 11.7$ for the CSH-S coated QCM sensor. And the fitting coefficients ($R^2$) was 0.9970.

We then calculated the limit of detection (LOD) and the limit of quantification (LOQ) of the CSH-S coated QCM sensor. The LOD and the LOQ were calculated using the Equations 4 and 5, respectively:

$$\text{LOD} = 3.3\sigma/S \quad (4)$$
$$\text{LOQ} = 10\sigma/S \quad (5)$$

where, $\sigma$ represents the standard deviation of the blank signal, and S represents the slope of the calibration curve. Using the above two formulas, the theoretical LOD was 0.0215 ppm, and the theoretical LOQ was 0.0652 ppm, respectively.

Fast response/recovery time is an important indicator to evaluate gas sensors. Figure 4c shows the response and recovery curve of CSH-S coated QCM sensor to 0.1 ppm gaseous aniline. The response/recovery time of CSH-S coated QCM sensor to gaseous aniline was calculated to be about 14 s/16 s, indicating the excellent response/recovery speed.

Figure 5a presents the repeatability of CSH-S coated QCM sensor to various concentrations of gaseous aniline. The CSH-S coated QCM sensor was sequentially exposed to 0.1 ppm, and was recovered after each cycle. The three continuous frequency shift curves to the same gaseous aniline concentration are almost the same, indicating that CSH-S coated QCM sensor has excellent repeatability. Besides, to explore the long-term stability, we tested the frequency shift of CSH-S coated QCM sensor to gaseous aniline of 0.1, 0.25, 0.5, 1 and 2 ppm within one month, as shown in Figure 5b. The frequency shift of CSH-S coated QCM sensor to gaseous aniline did not fluctuate significantly over one month, which confirmed favorable long-term stability.

The selectivity of CSH-S coated QCM sensor was evaluated by exposure to 0.5 ppm of six kinds of interference gases at 298 K, including CO, NO$_2$, NH$_3$, H$_2$, O$_2$, and HCHO, as shown in Figure 6a. The frequency shift of this sensor to gaseous aniline is obviously higher than other interference gases. In addition, we tested the frequency shift of the CSH-S coated QCM sensor to a mixed gas containing 0.5 ppm aniline and the above interference gases, as shown in Figure 3S. The sensor’s frequency shift to 0.5 ppm aniline showed no significant variations. We also conducted tests on three common aniline derivative compounds, namely N,N-diethylaniline, N,N-diphenylalaniline, and N,N-dimethylaniline. The concentrations of these three vapors were all set at 0.5 ppm. As shown in Figure 4S,

Table 1. Results of previous work

<table>
<thead>
<tr>
<th>Reference</th>
<th>Materials</th>
<th>Response/recovery time</th>
<th>Limit</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>UIO-66(OH)$_2$</td>
<td>135 s/74 s</td>
<td>100 ppb</td>
<td>2022</td>
</tr>
<tr>
<td>11</td>
<td>1,2,4-triazole functionalized UIO-66</td>
<td>4.3 min/2.8 min</td>
<td>1 ppm</td>
<td>2022</td>
</tr>
<tr>
<td>12</td>
<td>carbon nanocage/PMMA film</td>
<td>not given</td>
<td>3 ppm</td>
<td>2013</td>
</tr>
<tr>
<td>23</td>
<td>carboxylated cellulose aerogel</td>
<td>13 s/8 s</td>
<td>1 ppm</td>
<td>2022</td>
</tr>
</tbody>
</table>
the CSH-S coated QCM sensor response to 0.5 ppm aniline was significantly higher compared to the vapors of the three derivatives.

As shown in Figure 6b, it is nonnegligible to evaluate the anti-interference ability of BTEX vapor during the process of gaseous aniline sensing, including benzene, toluene, ethylbenzene, and xylene vapor. The concentration of the five gases is set at 1 ppm. The frequency shift of CSH-S coated QCM sensor to gaseous aniline, benzene vapor, toluene vapor, ethylbenzene vapor, and xylene vapor were −76.3, −6.5, −7.4, −8.1 and −6.9 Hz, respectively, indicating its selective detection ability to gaseous aniline against BTEX vapor. It should be attributed to the hydroxyl groups of CSH-S. Hydroxyl groups can interact with amino groups in aniline via hydrogen bond adsorption. Besides, the CSH-S coated QCM sensor was exposed to a gaseous aniline mixed with four interfering BTEX vapors to further assessment, including benzene, toluene, ethylbenzene, and xylene. Although the frequency shift increased (~79.1 Hz), the increase was not significant, indicating favorable selectivity against various interfering BTEX mixtures. By contrast, the frequency shift for four interfering BTEX vapors mixture (~12.8 Hz) is very small than that of aniline vapor (~76.3 Hz). These research results show that CSH-S coated QCM sensor possesses advantage of resistance to BTEX vapor.

Figure 4. (a) Dynamic frequency shift curve of CSH-S coated QCM sensor when exposed to gaseous aniline; (b) fitting curve of CSH-S coated QCM sensor with different gaseous aniline concentrations; (c) response/recovery time of CSH-S coated QCM sensor to 0.1 ppm gaseous aniline

Figure 5. (a) Repeatability of the CSH-S coated QCM sensor exposed to gaseous aniline at 0.1 ppm; (b) long-term stability of CSH-S coated QCM sensor to gaseous aniline

Figure 6. (a) Selective tests of CSH-S coated QCM sensor to 0.5 ppm of various detected gases at 298 K; (b) the comparison of frequency shift of CSH-S coated QCM sensor to five kinds of vapor (the concentration was set as 1 ppm). Frequency shift data showing the selectivity of CSH-S coated QCM sensor when exposed to gaseous aniline and interferent BTEX vapors with the concentration of 1 ppm
**Thermodynamic study of the sensor to gaseous aniline**

The frequency shift of the QCM based gas sensor originates from the change of the gas mass, which is caused by the adsorption between the target gas and the sensing material.\(^\text{25}\) The adsorption enthalpy (ΔH) was extracted to determine the selectivity and reversibility of adsorption process.\(^\text{26}\) Figure 7a shows the frequency shift of CSH-S coated QCM sensor to various concentrations of gaseous aniline at 298 and 313 K. The frequency shift of CSH-S coated QCM sensor declined with the increase of temperature, indicating the gaseous aniline adsorption exhibits negative Arrhenius temperature dependence. Figure 7b listed two isotherms, which express the relation between the uptake of gaseous aniline and the partial pressure of gaseous aniline at 298 and 313 K. According to Clausius-Clapeyron equation, ΔH was calculated to be −28.52 kJ mol\(^{-1}\) (showcased in the supplementary material). Many scientists\(^\text{25}\) report that the reversibility of sensors is satisfactory when ΔH is between 0 and −40 kJ mol\(^{-1}\), so the absorption sensing process of CSH-S coated QCM sensor for gaseous aniline can be considered as reversible, which is consistent with the above sensing test results.

Exploring the interaction between sensing materials and target gas is an effective way to study the sensing mechanism.\(^\text{27}\) The hydrogen bond adsorption of hydroxyl group and amino group in aniline can promote the sensing process.\(^\text{10}\) However, there are two different hydroxyl groups in CSH-S, including Ca−OH and Si−OH,\(^\text{17}\) as shown in Figure 8. It is very hard to select experimental method to explore their roles in the gaseous aniline-sensing process, so we choose the method of simulation calculation.

Gaussian 09 software is used to carry out the corresponding simulation calculation.\(^\text{24}\) Both hydroxyl groups in CSH-S, Ca−OH and Si−OH, can adsorb with amino group in aniline molecule. The thermodynamic parameters of the above adsorption processes were simulated. As shown in Figure 9, the enthalpy variation can be extracted as ΔH\(_1\) = −29.61 kJ mol\(^{-1}\) and ΔH\(_2\) = −26.37 kJ mol\(^{-1}\). The above two adsorption enthalpy data indicate that all two hydroxyl groups of CSH-S play a role in the sensing process, but Ca−OH is more important for detecting gaseous aniline. In addition, the Gaussian calculations also provide the entropy changes (ΔS) and Gibbs free energy changes (ΔG) for two reactions, which are as follows: ΔS\(_1\) = −17.53 J (K mol\(^{-1}\)), ΔS\(_2\) = −16.47 J (K mol\(^{-1}\)), ΔG\(_1\) = −24.38 kJ mol\(^{-1}\), ΔG\(_2\) = −21.46 kJ mol\(^{-1}\). The values of both ΔG\(_1\) and ΔG\(_2\) are less than 0 indicates that the adsorption reactions proceed spontaneously.

**CONCLUSIONS**

In summary, the facile loading of commercial calcium silicate hydrate nano sheets on the QCM platform made the sensing process of gaseous aniline sensitive, selective, repeatable and stable. In
addition, the sensing mechanism and thermodynamic process were explored by combining experiments and theoretical calculations. The hydroxyl groups in the silicate hydrate nanosheets play a key role in the detection of gaseous aniline. This facile constructed sensor may be a potential candidate for the commercialization of aniline detection in the future.

SUPPLEMENTARY MATERIAL

In supplementary material, available on http://quimicanova.sbq.org.br as a PDF file, with free access, are presented the characterization process; Clausius-Clapeyron equation; schematic of the testing system; XRD pattern; frequency shift values of the characterization process; Clausius-Clapeyron equation; schematic

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