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QCM formaldehyde sensing probes: design and sensing mechanism

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Abstract :
Formaldehyde (HCHO) is a common indoor noxious gas that needed to be detected in real time. Quartz crystal microbalance (QCM) is a transducer, which can be modified by various chemical sensing probes to detect specific gases. There have been some studies on QCM HCHO sensor, but none of them explored and validated the HCHO sensing mechanism, which is crucial for the rational design of sensing materials. In recent years, we have designed a series of new sensing probes based on QCM to detect HCHO, including polydopamine (PDA) related materials and diamino diphenyl sulfone (DDS) related materials. Gaussian 09 software was used to simulate the sensing mechanism of Schiff base adsorption and hydrogen-bonding adsorption. Besides, we have made waterproof optimization for these probes to enhance their application potential.

Key words: QCM, sensing probes, formaldehyde sensor, sensing mechanism

Polydopamine (PDA) related probes for detecting Formaldehyde (HCHO)

PDA is a kind of green and non-toxic imino group (-NH) containing material. We first reported the hollow PDA nanotubes as QCM probes to detect HCHO based on the hydrogen bond adsorption between –NH and HCHO [1]. As shown in Fig. 1, dopamine molecules are self-assembled onto the surface of ZnO nanorod. Then, PDA nanotubes can be obtained by the removal of ZnO template. The sensing results show that the detection limit towards HCHO is lower than 100 ppb. Based on Gaussian software, enthalpy change (ΔH) is obtained as -55.47 kJ/mol, which indicates that the interaction between PDA nanotubes and HCHO belongs to typical hydrogen-bond linking.

However, we found that the hydrophilicity of PDA makes it easy to induce false alarm in high humidity. Superhydrophobic polymerized n-octadecylsiloxane (PODS) nanostructure is used to cover the surface of PDA film to overcome this shortcoming [2]. As shown in Fig. 2, compared with pristine PDA based QCM sensor, the sensor based on PODS-PDA composite sensing probe shows satisfactory performance on avoiding false response and long-term stable formaldehyde sensing properties. This novel strategy offers a new method to reduce probability of false response resulted from humidity change.

Diamino diphenyl sulfone (DDS) related probes for detecting HCHO

Previously, DDS was not a member of the sensitive probe family. Recently, we have synthesized a novel complex by using DDS and methanol as the ligands as QCM probes to detect HCHO based on the Sciff base adsorption between amino group (–NH_2) and HCHO [3]. As shown in Fig. 3, we employ a physical vapor deposition (PVD) method to coat a thin layer of copper on the surface of QCM silver electrode. Then, a novel metal complex as HCHO sensing material is grown in-situ on the copper layer to ensure a strong coupling between metal complex sensing materials and QCM electrode. The detection limit reaches down to 50 ppb. Moreover, the calculations of ΔH between DDS ligand (-43.36 kJ/mol), methanol ligand (-2.80 kJ/mol) and HCHO molecule were obtained by using Gaussian software to verify the key role of DDS ligand.

Similarly, in order to enhance the water resistance of DDS probe, we using octadecylisothiocyanate and DDS as reactants a novel hydrophobic organic dry-gel named diamino diphenyl sulfone (DDS) urea for detecting HCHO [4]. The sensor based on this

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dry-gel urea probe can stable detect HCHO in different humidity. It should be attributed to the hydrophobic 18-carbon long chain. As shown in Fig. 4, Gaussian simulation results indicating that Schiff base adsorption between the $–NH_2$ and HCHO (-59.3 kJ/mol) is more responsible for HCHO sensing instead of hydrogen bond interaction between carbamido and HCHO (-28.5 kJ/mol).

In conclusion, We expound our idea of designing sensing probes. And put forward an stratery that understanding the sensing mechanism is important to designing expectant sensing probes properly. Besides, the combination of chemical experiment and simulative calculation can make the research more accurate and interesting.

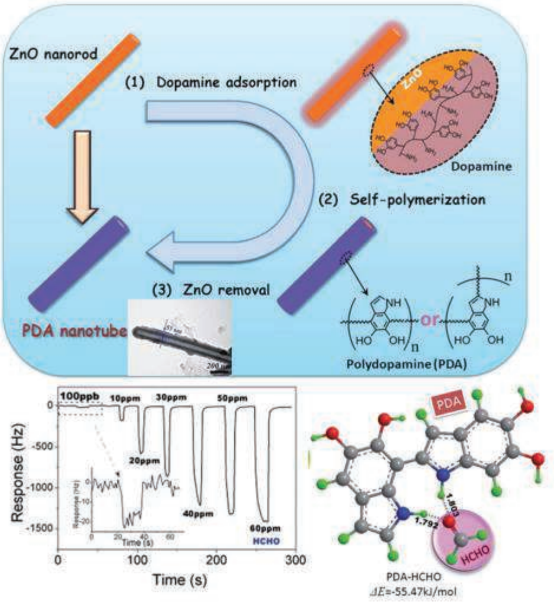

Fig.1 PDA nanotubes based QCM snesor for detecting HCHO and its sensing mechanism.

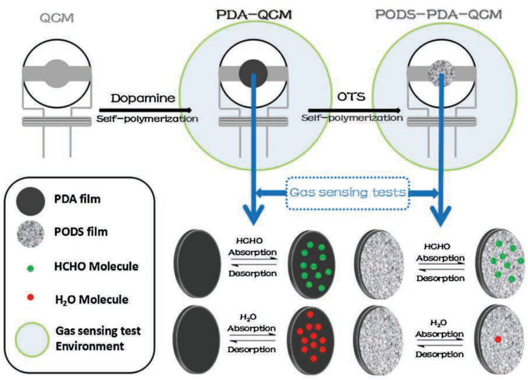

Fig.2 Scheme of the experiment we design for PDA based HCHO sensor to avoid humidit false response.

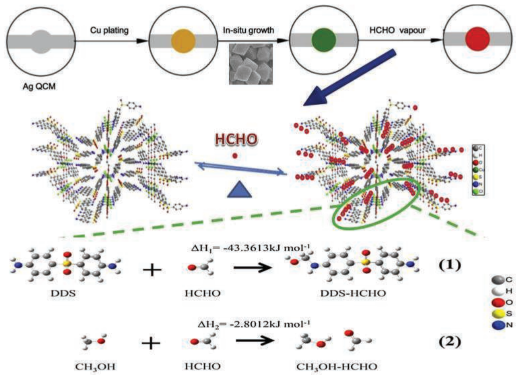

Fig.3 Scheme of the fabrication process of the complex based QCM gas sensor via situ growth method and specific capturing mechanism of HCHO molecules.

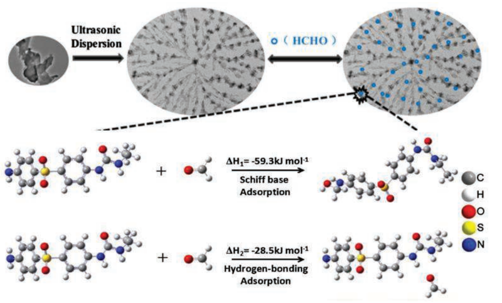

Fig.4 Scheme of the DDS urea dry-gel and adsorption mechanism of HCHO molecule.

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