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# QCM formaldehyde sensing materials: Design and sensing mechanism

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ABSTRACT

Gaseous formaldehyde (HCHO) sensing is indispensable because HCHO is hazardous to health and widely exists in newly decorated house and newly painted furniture. Multitudinous HCHO sensors based on various platforms, such as semiconductor sensor, electrochemical sensor, surface acoustic wave sensor (SAW), fluorescent sensor, have been fabricated over the last few years. Except these sensors, quartz crystal microbalance (QCM) sensors have received increasing attention because of their high sensitivity, convenient operation, low energy consumption, and excellent modifiable property. Recently, based on QCM, many efforts have been made to design chemical sensing materials to detect HCHO gas sensitively and selectively. In this review, we summary the scientific researches of gaseous HCHO detection based on QCM platform, and introduce the related works of sensing HCHO carried out by our group as well as the exploration of sensing mechanism.

## 1. Introduction

Formaldehyde (HCHO), a colorless gas at room temperature, was discovered by Hoffman in 1876 [1]. In recent years, people are terrified about HCHO, because it has become the top indoor harmful killer [2]. The adverse effects of HCHO are mainly reflected in the following aspects, as shown in Fig. 1 [3–5]. First, the skin, mucosa and respiratory tract will be strongly stimulated when instantly exposed to HCHO with high concentrations. People who has been exposed to HCHO may experience coughing, dyspnea, headache, fainting, or even death. Second, HCHO triggers a variety of allergic reactions. Respiratory tract inhaling a certain amount of HCHO may induce bronchial asthma, severe edema of respiratory tract, abnormal immune function, liver and lung injury, etc. When pregnant women are chronically exposed to HCHO with low concentrations, they will also cause fetal deformities and necrosis due to allergic reactions. Most seriously, HCHO induces gene mutations. Researchers have demonstrated in animal experiments that continuous exposure to HCHO can lead to an increase in the incidence of many kinds of tumors. The terrible HCHO gas is always existing in the lives of human beings, and its indoor sources are commonly founded. Indoor HCHO is difficult to remove in a short period of time, and it will release slowly for a long time, then cause great trouble to family life [6]. HCHO pollution was not so serious in the days when interior decoration was relatively primitive. Nowadays, people have the perfect pursuit for the decoration of houses and take various colorful decoration into the interior, but some toxic and harmful gases such as formaldehyde follow unavoidably. The sources of indoor HCHO can be roughly divided into three categories: man-made boards, paint coatings and some common indoor items, including wallpaper, chemical fiber carpets, textiles, etc [7–9]. In order to increase the crease resistance, the waterproofing and the fire resistance of textiles, factories must use some HCHO additives [10]. Therefore, people pay great attention to the real time detection of gaseous HCHO.

According to the physical and chemical properties of HCHO, it can be detected by some physical and chemical methods, such as colorimetry, fluorescence spectrophotometry, chromatographic analysis and so on [11–13]. These methods are very accurate in the detection of HCHO with low concentration. However, the disadvantage of these methods is that gaseous HCHO sample needs to be collected and processed in the laboratory before they can be detected. Besides, the operations of these tests are very tedious and need a long time. At the same time, professional technicians are required to operate these equipment's to provide reliable data results. These methods are far from meeting the requirement of real-time, continuous, and rapid HCHO detection. To achieve real-time and rapid detection, we must use the HCHO sensors based on sensor technology. Sensor technology has made great progress in recent years, and its development prospect are promising [14,15]. More and more scientists have devoted themselves to the scientific research of sensor technology in the field of harmful gases detection [16]. This upsurge is reflected in the increasing number of

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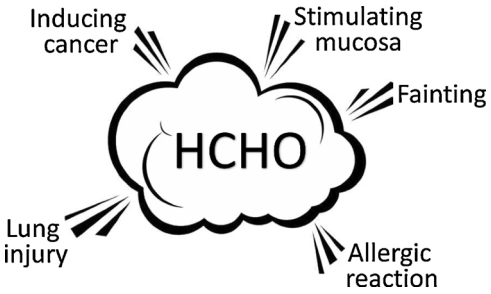


**Fig. 1.** Possible risks to humans caused by formaldehyde.

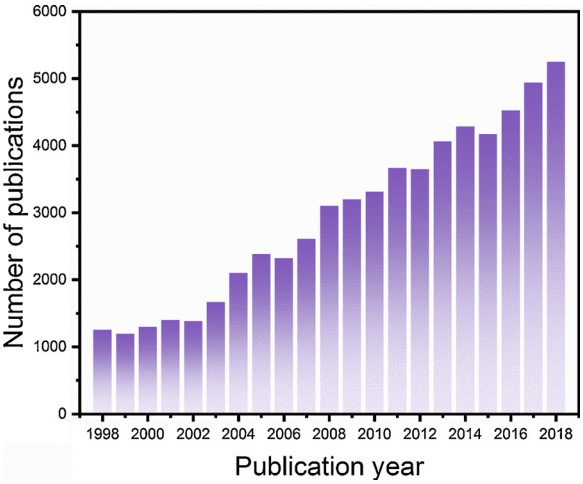


**Fig. 2.** The number of publications in the area of gas sensors from1998 to 2018 (internet search of the Scopus on Feb. 22, 2019). Keywords for search: gas sensor.

articles published particularly in the past few years, as shown in Fig. 2.

There are a wide variety of gas sensors, including fluorescent sensors, electrochemical sensors, chemiresistive sensor, etc. [17]. As the most commercialized one, numerous papers on chemiresistive sensors with metal oxides, 2D transition metal dichalcogenides, graphene and other nanomaterials have been published. Many gases have been tested and the detecting limits vary widely. For example, reduced graphene oxide flakes based sensors can reach 800 ppm for $NH_3$ gas [18]. Chemiresistive sensor based on molybdenum disulfide thin films can detect NH3 at 300 ppb concentration contrastively [19].

Gas sensors are required to work with high sensitivity and selectivity to meet the demands of various applications. So far, some strategies to improve the sensitivity and selectivity of sensing materials have been developed. The strategies to improve selectivity include designing heterostructures, surface functionalization, utilization of zeolite, fabrication of nanocomposite, etc. [20–22]. Recently, scientists reported that the selectivity and sensitivity can be improved by using binary metal oxides and hierarchical metal oxides, such as $BaCoO_3$, thick film, hierarchical $NiCo_2O_4$ platelets, yolk-shelled $ZnCo_2O_4$ microspheres, etc. [23–25]. Wang and coworkers reported that hierarchical Cr-doped $WO_3$ microspheres can detect hydrogen sulfide ($H_2S$) gas with higher selectivity and sensitivity than $WO_3$ microspheres. The hierarchical structures of hierarchical Cr-doped $WO_3$ microspheres provide a $H_2S$ gas diff ;usion path via well-aligned micro-, meso-, and macroporous architectures, resulting in significant enhancement in sensing response. Besides, the improved selectivity can be attributed to the increases in oxygen vacancies in $WO_3$ microspheres by Cr doping [26].

Based on sensing materials, some related commercial technologies have been created to detect gases, such as exhalation detector and electronic nose, etc. [27,28]. Nowadays, with the development of science and technology, scientists begin to pay attention to the miniaturization and portability of gas sensors, and develop some micro-electro-mechanical system (MEMS) gas sensors [29,30]. The detection limit of current gas sensors is a few ppb, hence, improving the detection limit to ppt levels represents a significant development [31].

Especially, in recent years, the problem of gaseous HCHO pollution has become serious. Air quality has been the focus of public attention, and the convenient detection of daily air quality has been greatly required. In order to meet the needs of the market, many sensors have been developed to detect HCHO, including conductometric sensors, interdigital electrodes (IDE) sensors, organic thin film transistor (OTFT) sensors, quartz crystal microbalance (QCM) sensors, etc. [32–35]. Conductometric sensor is the most classic sensor, and can well detect HCHO taking into account selectivity, sensitivity, and detection limits. But conductometric HCHO sensors usually need to work with the help of high temperature or ultraviolet irradiation [36,37]. As a contrast, HCHO sensors based on QCM can work stably at room temperature. The reported IDE sensors and OTFT sensors also detect HCHO at room temperature, but their gold-containing mechanical components are expensive [38]. By contrast, the electrode type of QCM is varied, and low-cost silver electrode can also achieve favorable HCHO sensing performance.

QCM is one quality testing platform based on piezoelectric effect of quartz crystal. It is sensitive to detect quality change in a nanogram (ng) level [39]. Its application fields include enzyme detection, gas phase measurement, and so on [40,41]. In 1959, Professor Sauerbrey discovered the relationship between the resonance frequency of quartz crystal oscillator and the mass change of crystal surface, which was named as Sauerbrey equation. It was proved that the frequency change of quartz crystal oscillator is proportional to the increase of surface mass [42]. Based on Sauerbrey equation, scientists can make QCM possess a special selectivity to different target gases. The method is modifying the surface of QCM by using various sensing materials [43–45]. As shown in Fig. 3, the sensing materials can selectively adsorb various harmful gases. The adsorbed gas molecules can change the quality of the device, then cause the oscillation frequency change of QCM. Therefore, as a gas sensor platform, QCM has great application potential and important application value. At present, researches and applications of QCM gas sensors have covered wide scopes, such as humidity, mercury vapor, toluene vapor, ammonia, alcohol, hydrogen cyanide, methylene chloride [45], trimethylamine, dimethoxymethylphosphine (DMMP), etc. [46–53]. QCM gas sensors have many advantages, such as high sensitivity at ng level, quantifiability for gas concentration, gas discriminability with e-nose, tunable selectivity, low power consumption, and so on [54]. Besides, QCM sensors are convenient to set up, operate and intelligentialize [55]. These advantages greatly arouse the interest of researchers in various countries, and make QCM sensors become a hot topic in the field of gas sensors. However, sensors based on QCM have obvious limitations. The stability of baselines is easy to be disturbed by the fluctuating environment and environmental humidity [35]. Besides, the selectivity of some QCM based sensors is difficult to meet the demand of users. For example, Li and

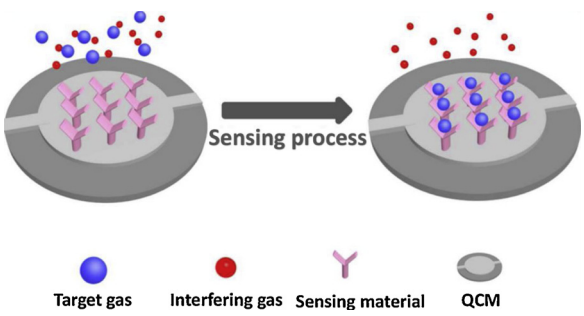


**Fig. 3.** The sensing process of the gas sensors based on QCM.

**Table 1**
Room-temperature HCHO-sensing properties of various sensing materials based on QCM.

| Reference | material | Sensitivity | Response/recovery time | Limit of detection |
|---|---|---|---|---|
| [35] | PODS-PDA | not given | 11 s/6 s | 1 ppm |
| [56] | copper (II) complex | not given | 9 s/11 s | 50 ppb |
| [57] | diphenyl sulfone urea dry-gel | not given | not given | 1 ppm |
| [60] | copper–manganese composite oxide | 6.35 Hz (mg ppm)$^{-1}$ | not given | 0.7 ppm |
| [62] | poly-dopamine functionalized hollow mesoporous silica spheres | not given | 5 s/3 s | 100 ppb |
| [65] | Graphene oxide | 22.9 Hz/ppm | not given | 0.06 ppm |
| [66] | Polyethyleneimine-multiwalled carbon nanotubes composite films | 0.82 Hz/ppm | 114 s/127 s | 0.6 ppm |
| [69] | Molecularly-imprinted polymer on a $TiO_2$ nanotube array | not given | 300 s/300 s | 1 ppm |
| [70] | PEI functionalized $TiO_2$ fibers | not given | 120 s/not given | 1 ppm |
| [75] | PEI/PVA | 0.5 Hz/ppm | not given | 10 ppm |
| [76] | PEI-PS | 1.7 Hz/ppm | not given | 3 ppm |
| [77] | PEI-PA 6 | not given | 150 s/not given | 50 ppb |
| [78] | PAN-PVA | not given | 120 s/not given | 500 ppb |
| [79] | PEI/BC | not given | not given | 1 ppm |
| [80] | Chitosan + PEI | not given | not given | 5 ppm |
| [82] | Amine-functionalized SBA-15 | not given | 11 s/15 s | 0.5 ppm |
| [85] | Polydopamine nanotubes | not given | 8.3 s/2.2 s | 100 ppb |

coworkers reported that polyaniline-$TiO_2$ composite based trimethylamine QCM sensor could detect 150 ppm trimethylamine, and the response was about 410 Hz. But, its response to 150 ppm triethylamine was about 320 Hz [52]. It is obvious that the difference in the two response values is not obvious.

Compared with traditional chemiresistive sensor worked at high temperature, the energy consumption of QCM sensor is lower, because QCM sensor usually works at room temperature [20,56]. In addition, it is difficult to predict sensitive materials for target gases for chemiresistive sensor researchers. On the contrary, based on QCM platform, scientists can actively design various materials containing different functional groups by referring to some reversible chemical reactions. Then, specific harmful gases could be detected expectably [57]. However, the favorable reliability, mature miniaturization, and moisture resistance of traditional chemiresistive sensor are widely recognized [58]. There is no doubt that these advantages are what QCM sensor needs to pursue.

In this review, we summarize the sensing materials for detecting HCHO based on QCM platform at room temperature, as illustrated in the parameters summarized in Table 1. These materials contribute to improving the sensitivity, selectivity, or repeatability of such sensors to HCHO gas. In order to further improve the sensing efficiencies, sensing materials can be modified. The configuration and sensing performances of HCHO sensors based on QCM was examined followed by discussing the sensing mechanism in detail. Our motivation is providing a detailed summary of all the published works on QCM based HCHO sensor, and presenting an outlook for the future development direction. The review has been divided into two sections, including sensing materials introduction and sensing mechanism discussion. We hope this review can provide a solid foundation for researchers to develop better HCHO sensor.

## 2. The QCM formaldehyde sensing materials

### 2.1. Oxides and oxide composites

Oxides, especially semiconductor metal oxides, are usually used in semiconductor gas sensors [59]. Besides, there are still some oxides that can be used for modifying QCM to detect HCHO. He et al. reported one HCHO sensor based on QCM by using a copper-manganese composite oxide at 20 °C [60]. Stacked copper-manganese composite oxide nanoparticles (25 mg) were modified on the electrode surface of a QCM chip by using a drop-coating method. The scanning electron microscope (SEM) image, transmission electron microscope (TEM) image and X-ray diffraction (XRD) pattern of the composite oxide demonstrated its amorphous property. The composite oxide modified QCM possessed an outstanding response (more than 150 Hz) to trace HCHO low to 0.3 ppm. After two months, the sensor's ability to detect 1.7 ppm HCHO was almost the same as the initial state. It should be attributed to the stability of the metallic oxide. There was a linear relationship between the response value of the QCM sensor and the concentration of HCHO, which made the copper-manganese composite oxide modified sensor have the ability to quantitatively detect HCHO.

Silica ($SiO_2$) is a resource-rich and low-cost oxide [61]. Hollow mesoporous $SiO_2$ spheres possess high surface area, abundant pore structure and adjustable surface properties. Zhu and coworkers used polydopamine (PDA) to functionalize hollow mesoporous $SiO_2$ spheres [62]. Then, the material was used to modify the electrode surface of QCM for detecting gasous HCHO. The detection limit of QCM sensor based on PDA functionalized hollow mesoporous silica spheres was 100 ppb. It had fast response speed (less than 5 s) and short recovery time (less than 3 s) with good sensitivity. In particular, the sensor was specially used in the rapid, sensitive, repeatable, and selective detection of artificially added HCHO released from some foods, such as mushrooms and broccoli.

Graphene oxide is the product of graphite powder after chemical oxidation and exfoliation [63,64]. Yang and coworkers developed a graphene oxide modified QCM sensor by drop-coating to detect HCHO [65]. The sensor had obvious response to HCHO and the sensitivity can reach 22.9 Hz/ppm. The sensing characteristics remained stable after one hundred days. In addition, the response of the HCHO sensor decreased with the decrease of HCHO concentration, so the sensor possessed the ability to quantitatively detect HCHO. All of these advantages made it possible for this sensor to be a suitable candidate for HCHO detection in the future. The sensing performance should be attributed to the hydrogen bonding adsorption between HCHO and the oxygen-containing functional groups on the surface of graphene oxide. Besides, another common carbon material, multiwalled carbon nanotube, was also used to detect HCHO after compounding polyethylenimide [66]. The volume ratio of multiwalled carbon nanotube to polyethylenimide was 1:1. Based on QCM platform, when the loading of the sensing material was 6521 Hz, the best sensing performance could be achieved. The response of the optimal sensor was approximately linear with the concentration of HCHO (within 6 ppm), the detection limit was 0.6 ppm, and the response time was about 1 h.

Titanium dioxide ($TiO_2$) is a classical oxide, which has a wide range of applications, such as pigments whitening and photocatalysis [67,68]. In the field of gas sensor, scientists have synthesized some $TiO_2$ based oxide composites to modify QCM for detecting HCHO gas. Polypyrrole-based molecularly imprinted polymer was synthesized on $TiO_2$ nanotube arrays to improve the surface volume ratio and enhance the HCHO sensing performance of the polymer [69]. The polypyrrole based

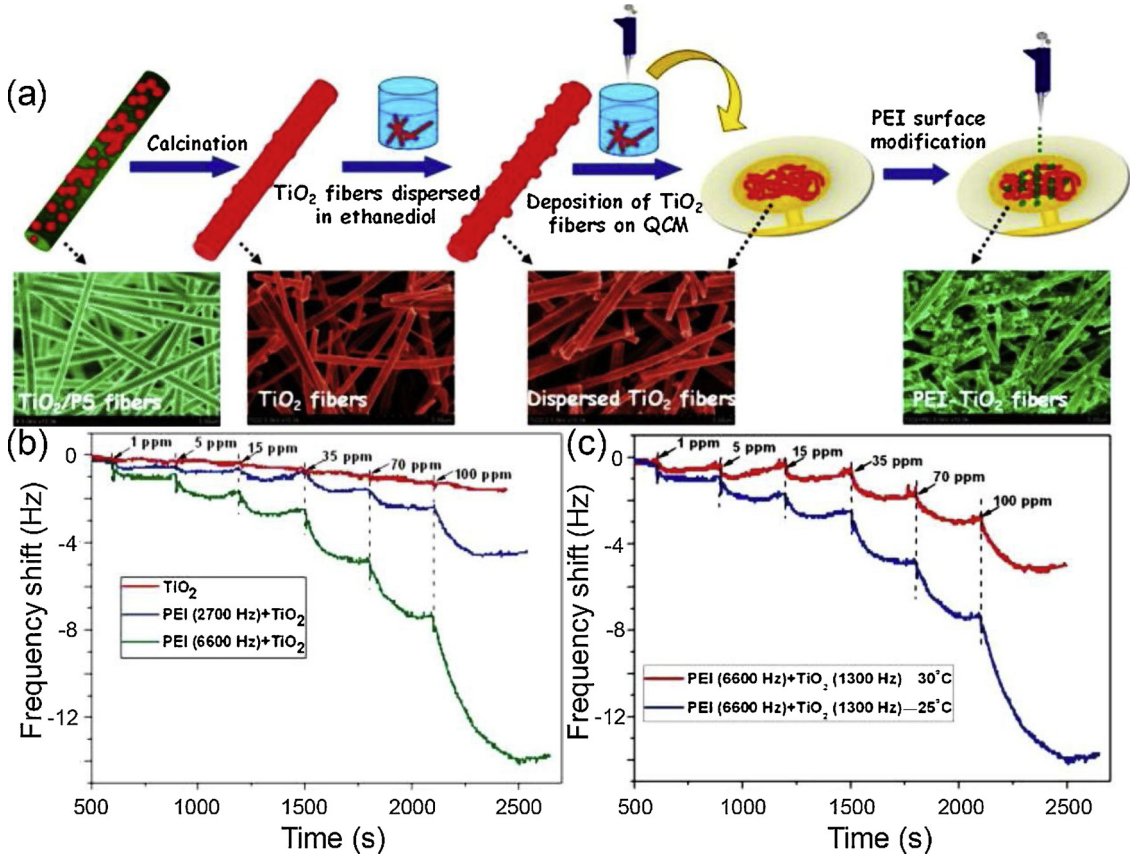


**Fig. 4.** (a) Schematic diagram illustrating the fabrication process and SEM images of the sensing layers on QCM. (b) Response of QCM-based PEI-$TiO_2$ sensors with different PEI coating loads (i.e. 0, 2700, 6600 Hz) upon exposure to increasing formaldehyde concentrations (1–100 ppm) at ambient temperature of 25 °C. (c) Effects of ambient temperature on the performance of the QCM-based PEI-$TiO_2$ sensors. The coating loads of PEI and $TiO_2$ were 6600 and 1300 Hz, respectively (Reused with permission from [70]. Copyright (2012) Elsevier).

molecularly imprinted polymer layer possessed a fish net structure with a thickness of 20 nm. The sensor selectively detected HCHO in ppm range at 22 °C. At the same time, the sensor could detect 5 ppm HCHO repeatedly for four times in 100 min, indicating its excellent repeatability. In addition, compared with some common interfering gases, the sensor had a good selectivity for HCHO.

Al-Deyab et al. prepared titanium tetraisopropoxide/polystyrene composite solution, and using it for electrospinning to fabricated nanoporous $TiO_2$ fibers with high specific surface area (68.72 $m^2$/g) followed by calcination process [70]. The $TiO_2$ fibers were then evenly dispersed in ethylene glycol solution, dropped on QCM electrode, and functionalized with polyethyleneimine (PEI), as shown in Fig. 4a. The SEM image in Fig. 4a showed that the diameter of the fiber was relatively uniform. As a highly sensitive sensing interface, $TiO_2$ fiber coated with PEI layer provided an output signal for the weight change of HCHO gas sensing process. As shown in Fig. 4b, the sensor had good detection ability to HCHO at 25 °C, including fast response and low detection limit (1 ppm). The response increased with the increase of HCHO concentration range of 1 ppm–100 ppm. Besides, as shown in Fig. 4c, increasing the temperature will decrease the response of the HCHO sensor.

The methods of molecularly printing and electrospinning mentioned above can be used to modify QCM quickly. Using metal oxides as HCHO sensitive materials usually requires the separate synthesis of nano oxides and subsequent sensor modification processes. There is no doubt that the process of manufacturing sensors needs to be simplified. Therefore, based on molecularly printing and electrospinning methods, we will introduce other QCM sensors for HCHO sensing.

### 2.2. Molecularly imprinted polymers

Molecularly imprinted polymers (MIPs) are characteristic polymers synthesized by molecular imprinting technology with specific recognition and selective adsorption to specific target molecules (template molecules) and structural analogues [71]. Obviously, this mechanism of selective adsorption makes MIPs have sufficient application potential in QCM gas sensing field. Feng et al. have demonstrated that molecularly imprinted polymers modified QCM platform can selectively detect HCHO molecules in low concentrations for the first time [72]. Because of the interaction between the molecular imprinting binding site and QCM substrate, the sensor had good sensitivity and selectivity to HCHO. This effective method has great potential in the construction of HCHO sensors.

Based the MIPs which were composed of styrene, methacrylic acid and ethylene glycol dimethacrylate on the surface of QCM, the detection limit of HCHO in dry air was 500 ppb [73]. Surprisingly, these MIPs exhibited excellent selectivity when tested other volatile organic compounds (VOCs) such as methanol, acetone, acetaldehyde, dichloromethane, and formic acid, and so on. Although MIPs are in principle suitable sensing materials, they are not useful for measurement at 50% relative humidity, because water saturates the polymers surface. This disadvantage was overcome via introducing amino groups into the MIPs and transforming the coating from thin film to nanoparticles. This optimization step allowed the HCHO sensor to maintain a selective detection limit of 500 ppb in the environment of 50% relative humidity.

Despite the fact that the above molecularly imprinted polymers have favorable HCHO sensing properties and quick manufacturing processes, they lack a stable structure and morphology. These

deficiencies will weaken the stability of HCHO sensors. Electrospinning technology can quickly modify stable polymer on the surface of QCM. These polymers prepared by electrospinning technology possess many gaps, which can provide more contact sites for gaseous HCHO molecules in theory.

### 2.3. Electrospun polymer nanofibers

The application of electrospinning technology in the study of various chemical materials can produce a wide variety of nanofibers, which have broad applied prospects [74]. Ding et al. used electrospinning technology to modify a series of electrospun polymer nanofibers on the surface of QCM substrate to detect HCHO, including nanfibrous polyethyleneimine membranes [75], polyethyleneimine functionalized manoporous polystyrene fibers [76], polyethyleneimine functionalized polyamide 6 composite nanofiber/net [77], polyvinylamine modified polyacrylonitrile nanofibers [78], nanofibrous polyethyleneimine/bacterial cellulose membranes [79], and polyethyleneimine modified electrospun nanofibrous chitosan membranes [80]. These nanofibers prepared by electrospinning technology possessed cross-linked network structures, large specific surface areas, high porosity and large packing density. These advantages made electrospinning nanofibers possess a reliable choice for sensing applications based on QCM. As a typical example, polyacrylonitrile nanofibers were modified onto the electrode surface of QCM by electrospinning technology followed by adding polyvinylamine (Fig. 5a). The SEM images of polyacrylonitrile nanofibers and polyvinylamine modified polyacrylonitrile nanofibers are shown in Fig. 5b and c, and the two polymers all possess cross-linked network structures. As shown in Fig. 5d, compared with polyacrylonitrile-polyvinylamine flat film, polyvinylamine modified polyacrylonitrile nanofibers possess higher response toward HCHO with the same concentrations. The selectivity of the HCHO sensor based on polyvinylamine modified polyacrylonitrile nanofibers was also excellent, because its response values to seven interfering gases are much less than that to HCHO at the same concentration. In brief, the QCM sensor can be obtained conveniently and directly by electrospinning technology. At the same time, there are many kinds of materials can be electrospun. As a result, many different types of QCM sensors can be invented theoretically.

### 2.4. Sensing materials designed by our research team

Based on QCM platform, our research team has also develop some novel HCHO sensing materials. Based on these works, a summary is given.

SBA-15 is a typical ordered mesoporous silica material [81]. We reported amino gruops functionalized SBA-15 with adjustable amino loading by post-grafting method [82]. The mesoporous structure of SBA-15 is beneficial to the grafting of amino groups in the pore and avoiding the grafting inhomogeneity in the pore. In addition, the amino functionalized SBA-15 maintained the excellent pore structure of SBA-15. A novel HCHO sensor with high sensing performance was constructed by using QCM as the transducer platform and amino functionalized SBA-15 as the gas sensing material. Amino-functionalized SBA-15 possessed a large specific surface area, which enabled the material to adsorb more HCHO molecules. As a result, the sensitivity of the sensor could be enhanced. Amino groups in amino-functionalized SBA-15 could react with HCHO molecules reversibly at room temperature by Schiff base adsorption, so the selectivity of HCHO sensing materials can be improved. The thermal stability of the synthesized material enabled itself to meet the requirements of practical application. This report not only developed an excellent HCHO sensing material, but also broadened the application field of mesoporous materials.

Previously, diphenyl sulfone was not a member of the sensing

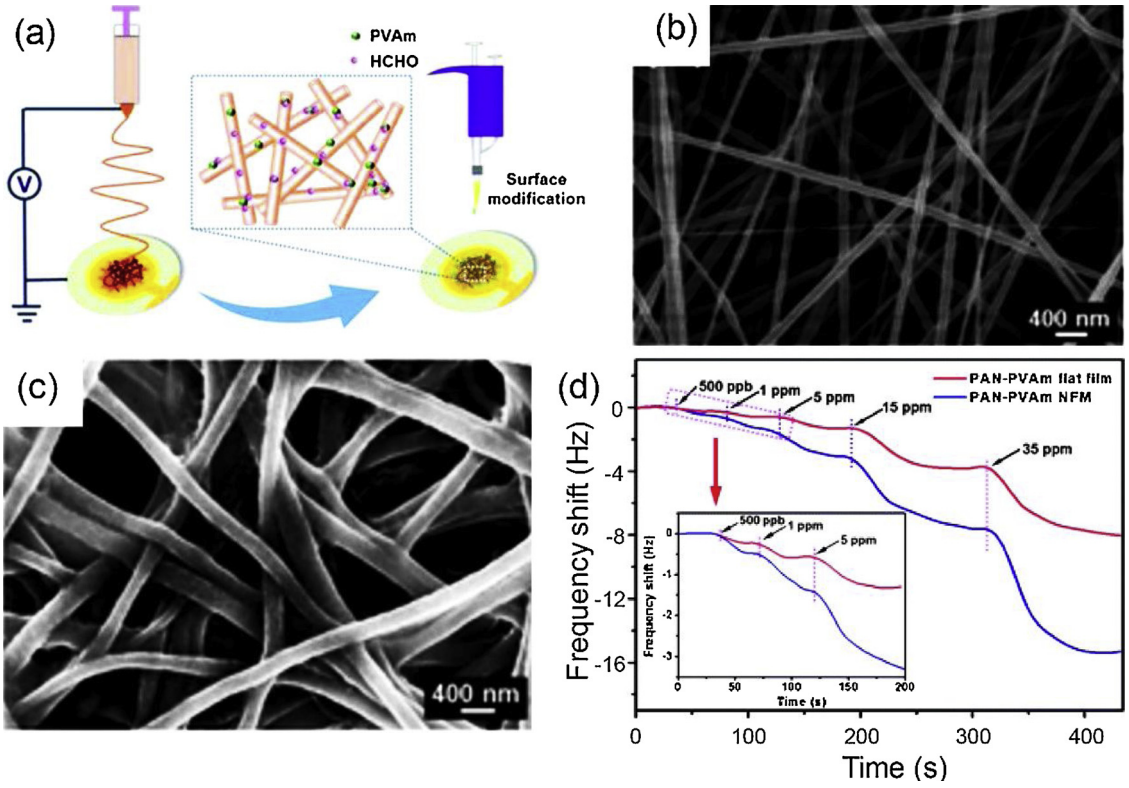


**Fig. 5.** (a) Schematic illustration for the preparation of sensing Polyacrylonitrile-polyvinylamine nanofibrous membrane coated on a QCM electrode. (b) SEM image of Polyacrylonitrile nanofibrous membrane. (c) SEM image of polyvinylamine modified Polyacrylonitrile nanofibrous membranes. (d) Dynamic response of QCM sensors coated with two different sensing structures upon exposure to increasing formaldehyde concentrations. Inset is the amplified image for 0.5, 1, and 5 ppm formaldehyde detection (Reused with permission from [78]. Copyright (2013) Royal Society of Chemistry).

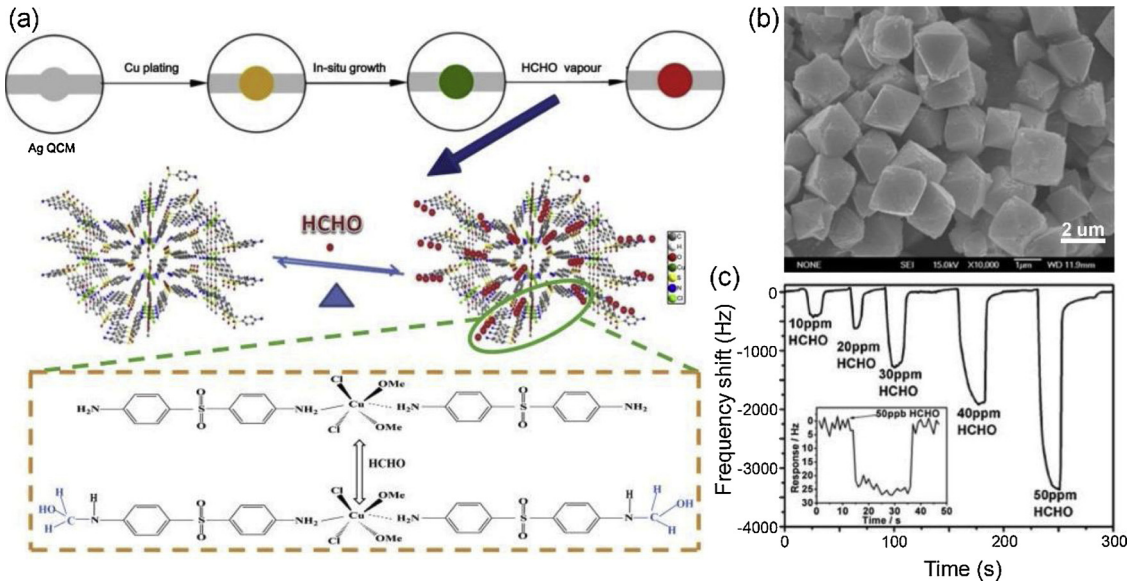


**Fig. 6.** (a) Scheme of the fabrication process of the complex based QCM gas sensor via situ growth method and specific capturing mechanism of HCHO molecules. (b) SEM image of the as-synthesized complex. (c) Typical sensor responses versus formaldehyde of various concentrations of 10, 20, 30, 40, 50 ppm, as well as 50 ppb at 298 K (Reused with permission from [56]. Copyright (2017) Elsevier).

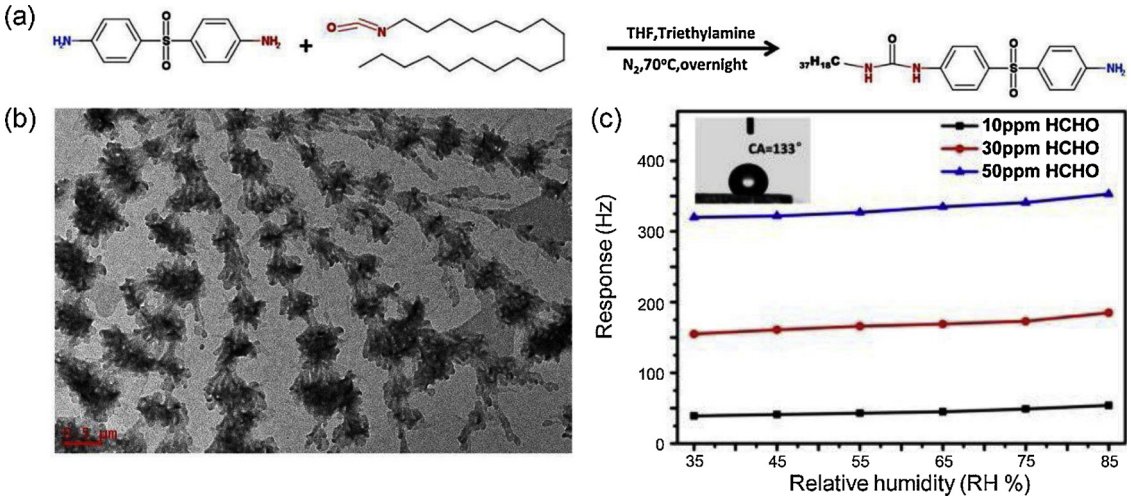


**Fig. 7.** (a) The synthesis process of the urea material. (b) TEM image of the dry-gel. (c) The frequency response of dry-gel based QCM sensor exposed to 10, 30, and 50 ppm of formaldehyde at some common relative humidity environments. The inset shows the contact angle image of dry-gel based QCM (Reused with permission from [57]. Copyright (2017) Elsevier).

material family. However, diphenyl sulfone has a stable structure and many various additional functional groups for different application purposes [83]. Recently, we synthesized a novel complex (named DDS-Cu) by using diamino diphenyl sulfone (DDS) and methanol as the ligands [56]. The complex was used as QCM probe to detect HCHO based on the Schiff base adsorption between the amino group of DDS ligand and HCHO. As shown in Fig. 6a, a physical vapor deposition (PVD) method was employed to coat a thin layer of copper on the surface of QCM electrode. Then, a octahedral metal complex (Fig. 6b), acting as HCHO sensing material, was grown in-situ on the copper layer to ensure a strong coupling between the sensing material and QCM electrode. As shown in Fig. 6c, the detection limit of the sensor for HCHO gas was lower than 100 ppb. In order to enhance the water resistance of DDS probe, we used octadecylisothiocyanate and DDS as reactants to synthesize a novel hydrophobic organic dry-gel, which was named as diamino diphenyl sulfone (DDS) urea for detecting HCHO, as shown in Fig. 7a [57]. As shown in Fig. 7b, the morphology of the dry-gel material is divergent chain stripe. Fig. 7c shows that the QCM sensor based on this hydrophobic dry-gel urea probe can steadily detect HCHO in different humidity. It should be attributed to the hydrophobic eighteen-carbon long chain.

Polydopamine (PDA) is a green and non-toxic imino group containing material [84]. We first reported the hollow PDA nanotubes (Fig. 8a and b) as QCM probes to detect HCHO based on the hydrogen bond adsorption between imino group and HCHO [85]. The synthesizing process is shown in Fig. 8c. Dopamine molecules are self-assembled onto the surface of ZnO nanorod firstly. 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 (Fig. 8d).

However, we found that the hydrophilicity of PDA makes it possible 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 [36]. As shown in Fig. 9a, this is a novel strategy. Compared with pristine PDA based QCM sensor, the sensor based on PODS-PDA composite shows better sensing

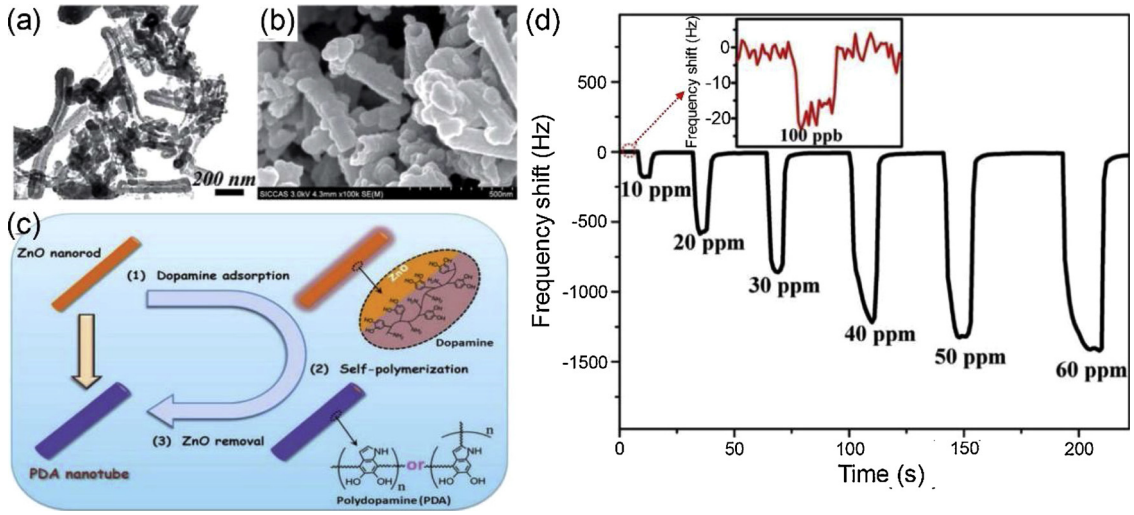


**Fig. 8.** (a) TEM image of the hollow PDA nanotubes. (b) SEM image of the hollow PDA nanotubes. (c) Roadmap of the synthesis procedure of hollow PDA nanotubes. (d) Real-time dynamic response curve of PDA based sensor exposure to HCHO with increasing concentration at room temperature. The inset shows the sensing response to 100 ppb HCHO (Reused with permission from [85]. Copyright (2016) Royal Society of Chemistry).

performance on avoiding false response (Fig. 9b) and more satisfactory long-term stable HCHO sensing properties (Fig. 9c). This novel strategy offers a new method to reduce the probability of false response resulted from humidity change.

In this section, all the HCHO sensing materials based on QCM platform have been introduced in detail, including oxides and oxide composites, molecularly imprinted polymers, electrospun polymer nanofibers, and novel sensing materials designed by our research team. The selectivity, sensitivity and detection limit of the sensors based on these materials are favorable. Besides, aiming at the disadvantage that some materials are easily affected by humidity, some improved treatments have been developed. These scientific advances provide a basis for further research on practical HCHO sensor. In addition to sensing performance exploration, the sensing mechanism is also important and instructive. Next we will summarize the progress that has been obtained in the sensing mechanism of QCM based HCHO sensors.

## 3. The sensing mechanism of QCM based HCHO sensors

In the field of chemical gas sensors, most of the current researches are focusing on the design and synthesis of materials, as well as the testing and evaluation of sensing performance. However, the research on sensing mechanism has not attracted enough attention. It is very necessary to study the sensing mechanism. Understanding the sensing mechanism can not only explain the working mechanism of the sensor, but also provide a basis for further design and optimization of sensing materials. In the past, in the field of QCM based HCHO sensor, the research on the sensing mechanism was mostly in the discussion stage based on the theoretical basis, and had not been verified by some practical methods. Our research team pioneered the use of experimental and simulation methods to study the sensing mechanism of QCM based HCHO sensor.

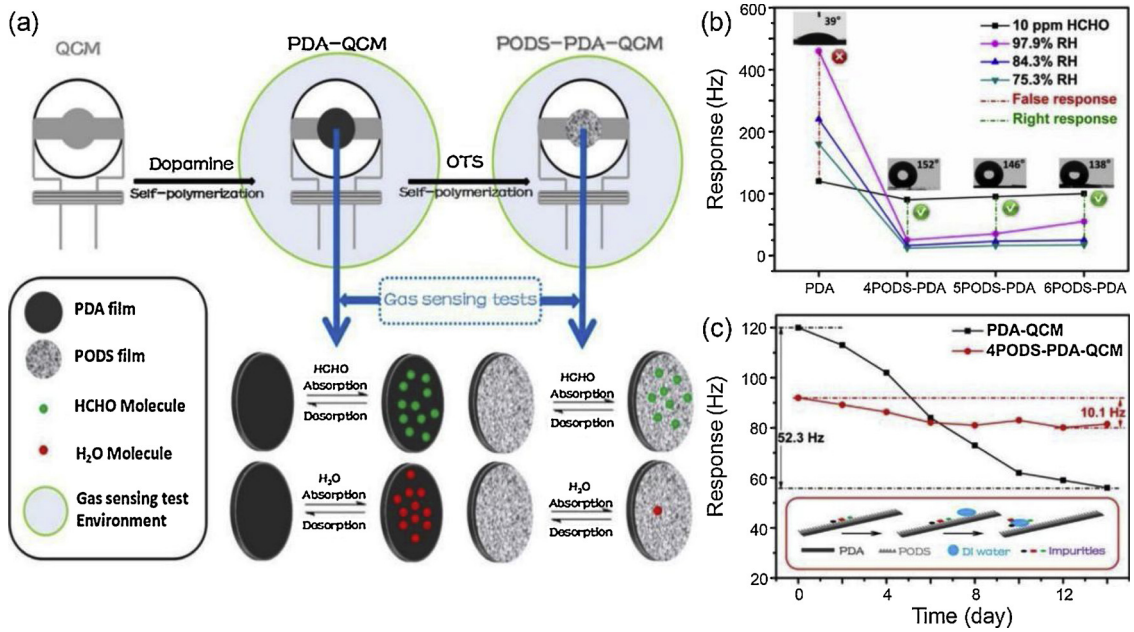


**Fig. 9.** (a) Scheme of the experiment we design. (b) False response region of PDA-QCM and right response region of PODS covering PDA-QCMs. (c) Sensing results are obtained with an interval of two weeks for evaluating long term stability of 4PODS-PDA-QCM towards 10 ppm HCHO. The inset shows the reason for long-term stability (Reused with permission from [35]. Copyright (2018) Elsevier).

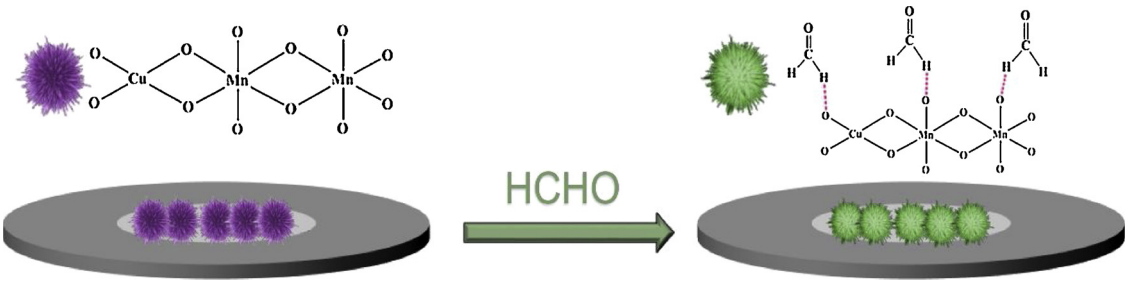


**Fig. 10.** Schematic illustration of the HCHO sensing mechanism of the as-prepared copper-manganese composite oxide.

### 3.1. Sensing mechanism based on chemical theory

QCM is a mass sensitive gas sensor. Theoretically, the interaction between the surface of a mass-sensitive chemical sensor and the molecule to be detected is the adsorption mechanism of gas molecules on the QCM surface. This adsorption is activated by intermolecular forces, such as classical hydrogen bonding and van der Waals interactions, to collect gas molecules on the surface of solid sensitive materials. For example, in view of the above mentioned copper-manganese composite oxide on HCHO sensing performance, researchers proposed its sensing mechanism based on traditional chemical theory [60]. As shown in Fig. 10, there are many oxygen atoms on the surface of copper-manganese composite oxide, which can interact with hydrogen atoms in HCHO molecules through hydrogen bond adsorption. Based on this theory, most metal oxides have abundant oxygen atoms on their surfaces, so they also have potential application in the area of HCHO sensing.

For graphene oxide, a large number of oxygen groups on its surface determine their HCHO sensing ability, such as carbonyl groups, hydroxyl groups, etc [65]. The surface of graphene oxide may adsorb HCHO molecules through reversible hydrogen bond adsorption or irreversible condensation reactions between functional groups and HCHO molecules. However, the response of graphene oxide to HCHO is completely reversible, so the existence of strong adsorption can be ruled out, which verified the dominant role of hydrogen bond adsorption in HCHO sensing process. Although the above mechanism analyses are consistent with the performances of the HCHO sensors, it is still limited to the theoretical level, and cannot thoroughly analyze the sensing mechanism at the experimental level. Next we will summarize some sensing mechanism of QCM based HCHO sensors obtained by experimental method.

### 3.2. Thermodynamic investigations of sensing materials for exploring sensing mechanism

Based on mass-sensitive sensors named resonant microcantilever, Li et al. systematically studied the thermodynamics and kinetics of gas adsorption on the surface of sensitive materials based on mass-sensitive sensors [86]. Based on the classical physical-chemical adsorption theory and Clausius-Clapeyron equation, they kept the ambient pressure constant and quantitatively calculated the adsorption enthalpy (ΔH) of the target gas molecule adsorbed by the sensing material using the difference in the response values at different temperatures (variable temperature experiments). Therefore, the adsorption modes between sensing materials and gases are classified qualitatively. As shown in Fig. 11, they proposed that when the ΔH of the sensitive material (mesoporous silica) to the target gas is larger than −40 kJ/mol, the adsorption mode of the material to the gas is physical adsorption, which can ensure the reversibility of adsorption-desorption, but lack of selectivity to the target gas. When the ΔH of the sensing material (−$SO_3H$ functionalized mesoporous silica) to the target gas is smaller than −80 kJ/mol, the adsorption mode of the material to the gas is chemical reaction, which can provide adsorption selectivity without reversibility. When the ΔH of the sensing material (−COOH functionalized mesoporous silica) to the target gas is between −80 kJ/mol and −40 kJ/mol, it is the most ideal interface adsorption mode. Under this adsorption mode, sensing material can adsorb target gas with selectivity and reversibility. This series of researches and theories undoubtedly provide a great help for researchers engaged in mass-sensitive gas sensors. Based on this series of theories, researchers can determine the adsorption mode of the interface between sensing materials and target gases through experimental data. As a result, researchers can be more targeted in the analysis of gas sensing mechanism and more purposeful in the design of gas sensitive materials.

QCM platform can also be used for similar research which is also a mass-sensitive gas sensing platform. Our research team have completed some researches in this field. As shown in Fig. 12, we calculated the ΔH (−53.6 kJ/mol) between HCHO molecules and hollow PDA nanotubes by using temperature change experiment and Clausius-Clapeyron equation, indicating that the adsorption mode is chemical adsorption [85]. Using the same method, we have calculated the ΔH values of HCHO adsorbed by DDS-Cu complex and DDS urea, which is −45.2 kJ/mol and −41.7 kJ/mol, respectively [56,57]. Obviously, the adsorption methods between HCHO and these two materials also belong to chemical adsorption. Therefore, the reversibility and selectivity of these two HCHO sensing materials are explained experimentally.

The above experimental method can be used to extract the adsorption enthalpy between sensing material and HCHO molecules. But the experiment always has slight and unavoidable errors. Therefore, some simulation calculations are needed to verify the reliability of the experimental results [87].

### 3.3. Gaussian simulation of sensing mechanism

The combination of calculation and experiment can make the experimental results more accurate and reliable [87]. In order to further explore the response mechanism of HCHO sensing materials, we introduced the quantum chemistry calculation method via using Ganssian 09 software for the first time to verify the experimental results. In the course of simulation calculation, the ΔH values in HCHO adsorption are calculated by simulating the binding of different sites in the sensing materials with HCHO, and the experimental results are verified theoretically.

The first material used to simulate the sensing mechanism using Ganssian 09 software is hollow PDA nanotubes mentioned in section 2.4 [85]. As shown in Fig. 13, hydrogen bond interaction is formed between two imino H atoms of the monomer and aldehyde O atom of HCHO molecule. After optimizing the configuration of reactants and product molecules, Ganssian 09 software carried out the following calculation result that the value of ΔH is −55.47 kJ/mol, which indicating that the HCHO molecule can form reversible chemical hydrogen-bond adsorption with PDA. Besides, the calculated result is close to the experimental one from the variable temperature experiment, thus achieving the consistency between the theoretical calculation and the experimental result.

In addition to the theoretical verification of the experimental result,

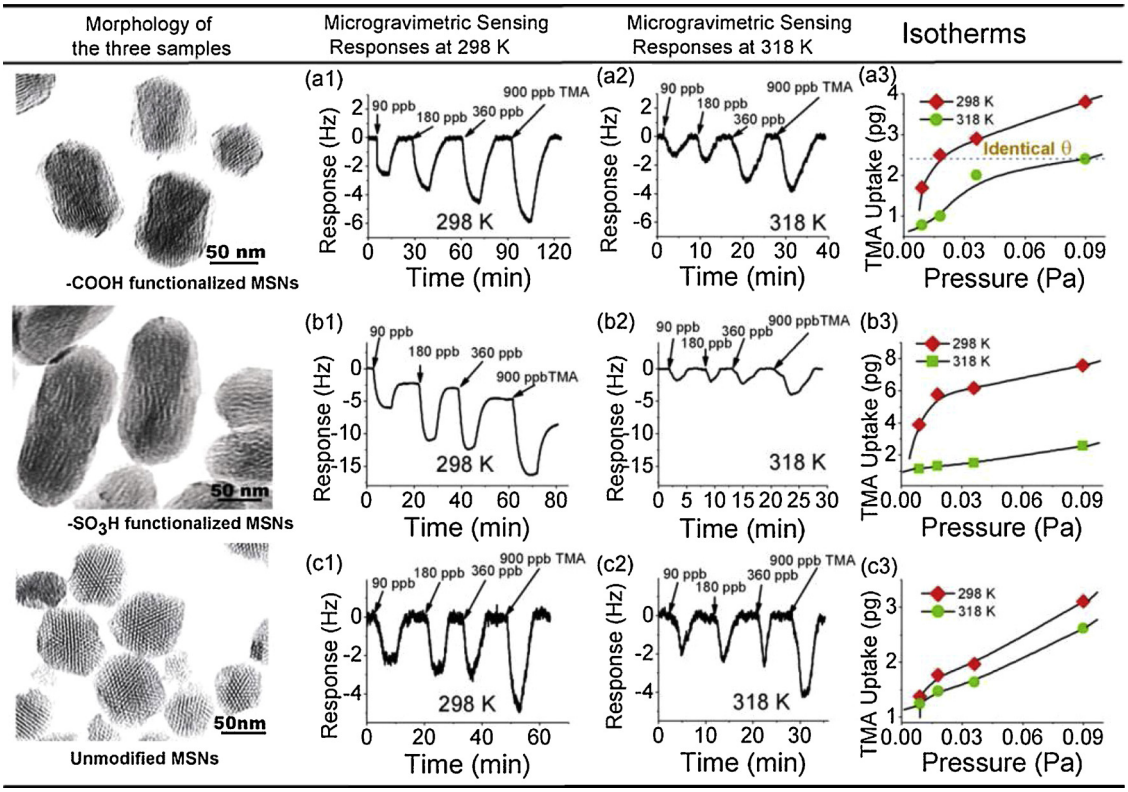


**Fig. 11.** TEM images of the prepared MSNs, adsorption induced gravimetric responses, and the isotherms of the MSN-loaded resonant-cantilever to TMA vapor of various trace-level concentrations are shown from left to right. The two experimental temperatures are 298 and 318 K. The top raw of (a1–a3) is for the −COOH-functionalized MSNs, the middle raw of (b1–b3) is for the −SO3H-functionalized MSNs, and the bottom raw of (c1–c3) is for the −OH-covered unmodified MSNs (Reused with permission from [86]. Copyright (2018) American Chemical Society).

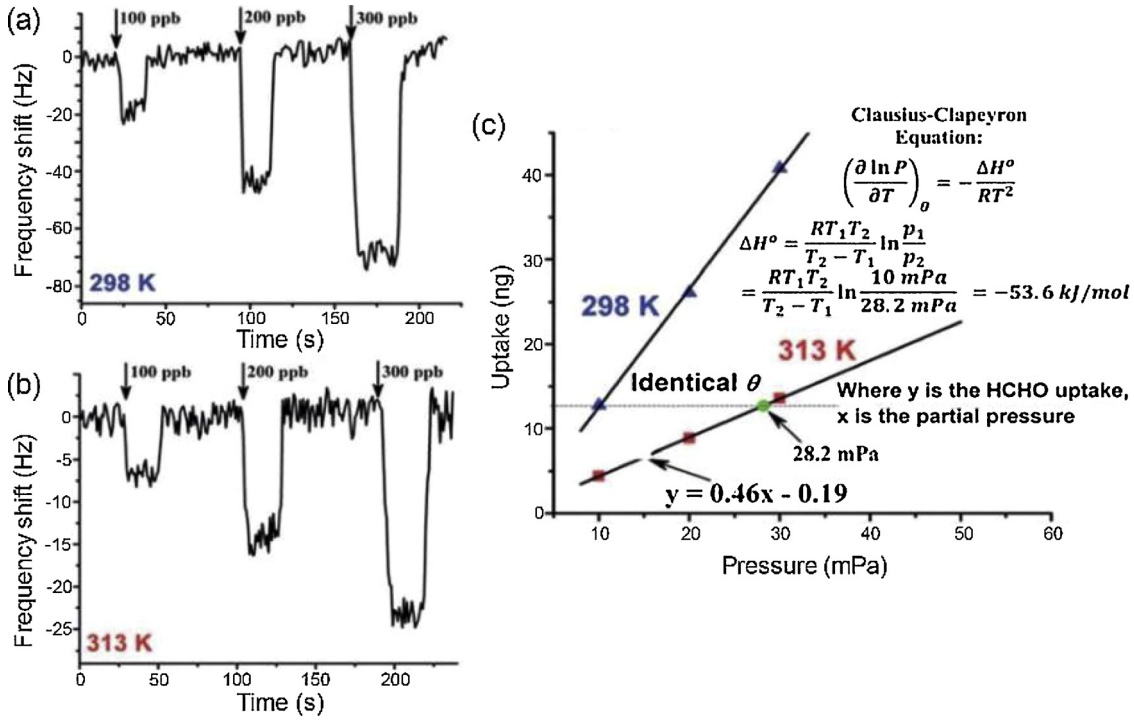


**Fig. 12.** Gravimetric curves of hollow PDA nanotubes based QCM at (a) 298 K and (b) 313 K to HCHO with different concentrations of 100, 200, and 300 ppb, respectively. On the basis of the temperature-varied micro-gravimetric curves, the plotted isotherms are used for extracting the thermodynamic parameter of ΔH, which is further used to evaluate the HCHO sensing properties of Cu-complex. (c) Based on the experimental results in (a) and (b), two isotherms are plotted to calculate the enthalpy change (ΔH) (Reused with permission from [85]. Copyright (2016) Royal Society of Chemistry).

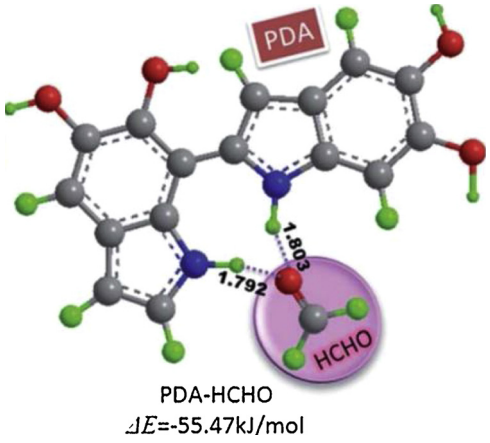


**Fig. 13.** Optimized geometries and the H-bonding interaction between the PDA monomer and formaldehyde molecule under study (Reused with permission from [85]. Copyright (2016) Royal Society of Chemistry).

Ganssian 09 software can finish more research. When HCHO can be adsorbed by several functional groups in single sensing material theoretically, experimental method is not able to judge the primary of the functional groups. For example, in addition to DDS ligand, complex mentioned in section 2.4 also has methanol ligand. In theory, methanol ligands can adsorb HCHO molecules by hydroxyl group. In order to obtain more accurate sensitive mechanism, our group utilized Gaussian 09 software to distinguish which ligand was dominating the HCHO sensing ability of the complex [56]. Fig. 14 shows two theoretical reactions about HCHO molecule and two ligands of the complex. Using Gaussian 09 software, we calculated the following two ΔH values of the two reactions: ΔH1 and ΔH2. The enthalpy change (ΔH1) of the reversible Schiff base adsorption between HCHO molecule and the $-NH_2$ group of DDS ligand (Fig. 14a) was calculated to be $-43.3613$ kJ/mol, indicating that the interaction mode is weak chemical adsorption. Contrarily, the enthalpy change (ΔH2) of the hydrogen bond adsorption between HCHO molecule and the $-OH$ group of methanol ligand (Fig. 14b) was calculated to be $-2.8012$ kJ/mol, which belongs to physical adsorption. Obviously, reaction 1 is easier to happen than reaction 2, and plays a more critical role in the process of HCHO detection.

Similarly, we utilized Gaussian 09 software to discover which group of the dry-gel mentioned in section 2.4 is the key in the HCHO sensing process [57]. Apart from -$NH_2$ group, the dry-gel also possesses carbamido, which can synergistically adsorb HCHO molecule by the two imino H atoms. In Fig. 15, the values of ΔH1 and ΔH2 can be simulated: ΔH1 = $-59.3$ kJ/ mol, ΔH2 = $-28.5$ kJ/ mol. Calculation results reveal that in this system, $-NH2$ group is more responsible to adsorb HCHO molecule by Schiff base interaction than carbamido.

## 4. Conclusion and outlook

In summary, the categories and sensing mechanism of HCHO sensing materials based on QCM were reviewed in detail. After the report of Sauerbrey equation in 1959, QCM based gas sensors have received wide attention owing to their outstanding sensing performance although the class of QCM based gas sensor is just a rookie of the chemical gas sensor team. Published works have demonstrated the advantages of low power consumption, high sensitivity and purposeful modification as compared with other traditional chemical gas sensors. This suggests that QCM based gas sensors could be exploited for applications in many areas where other gas sensors are not competent. Although QCM based HCHO sensor has attracted increasing attention, it not yet entered the mature stage. The stability and moisture resistance of HCHO sensing materials based on QCM are key points need to be addressed during the sensing process. HCHO sensing materials based on QCM must possess enough adsorption sites to adsorb HCHO. Besides, it is also necessary to fully understand the sensing mechanism of HCHO, which can optimize the design strategy and promote the development of HCHO sensor. This review provides the categories and sensing mechanism of HCHO sensing materials based on QCM by summarizing most of the reported studies.

In terms of the QCM platform for constructing HCHO sensors, the sensing materials of oxides and oxide composites, molecularly imprinted polymers, electrospun polymer nanofibers, novel sensing materials prepared by our research team, etc, are presented. All of these sensing materials are used in detecting HCHO with different properties successfully. In particular, our research team has finished some original ideas on improving the waterproof properties of HCHO sensing, including post-grafting hydrophobic functional group and covering superhydrophobic film, which widening the road for optimizing the HCHO sensors with the enhancement of stabilization and selectivity. However, these strategies of sensing HCHO are dependent on a limited variety of sensing materials. Thus, further exploration of widening the range of novel and environmental friendly HCHO sensing materials with better sensing performance is desirable.

Because of the strong desire to discover the detailed HCHO sensing mechanism, scientists in the field of QCM have made great efforts. Based on traditional chemical theories, scientists analyzed the structures of sensing materials and HCHO molecule to explore the theoretical ways of interaction. Recently, the enthalpy change between the sensing material and HCHO molecule was extracted by the variable temperature experiment and the simulated calculation. This synergistic study can not only explore the adsorption mode of HCHO molecule on sensing materials, but also identify the most important functional group in the material for HCHO sensing. However, similar studies are relatively rare. More in-depth researches are needed to discuss and explore the sensing mechanism of more HCHO sensing materials.

Despite the HCHO sensors based on QCM are promising, the difficulty of large-scale production hinders their industrial application prospect. Besides, the laboratory's measuring equipment of QCM is expensive. On the other hand, continuous production of the sensing

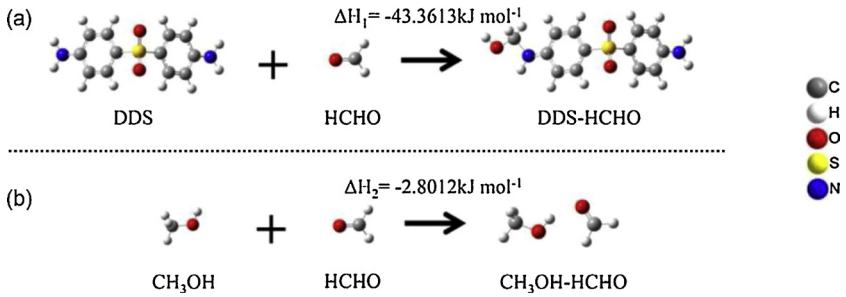


**Fig. 14.** Optimized geometries and interactions between HCHO molecule and ligands (a) DDS and (b) CH3OH (Reused with permission from [56]. Copyright (2017) Elsevier).

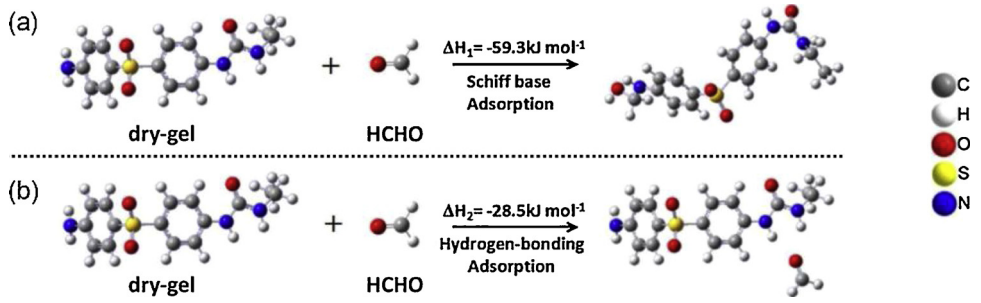


**Fig. 15.** The Gaussian simulations of Schiff base adsorption between HCHO molecule and dry-gel (Reused with permission from [57]. Copyright (2017) Elsevier).

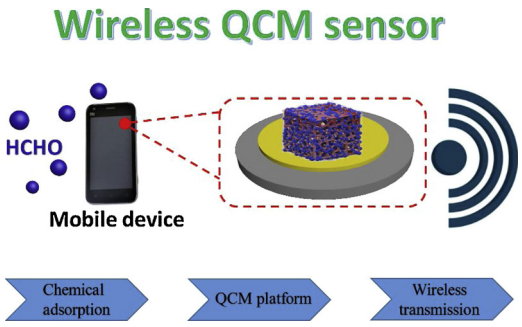


**Fig. 16.** The concept design of micro wireless QCM based HCHO sensors in the future.

materials mentioned in this review is challenging. Moreover, some compounds having similar chemical nature/properties, such as acetaldehyde and ethanol, could cause a lot of interference to HCHO sensor based on QCM. To solve these problems, some metal-organic frameworks (MOFs) materials may be available. MOFs are efficient materials for separation and adsorption [88,89]. Scientists have found that many similar small molecules can be separately adsorbed by using the diversity and tunability of the ligands and pore structure of MOFs [90,91]. We believe that by designing ligand with specific functional groups to adsorb HCHO and controlling suitable pore structure to fit the size of HCHO molecule, MOFs modified QCM sensors can selectively detect HCHO in the mixture of HCHO and other similar compounds in the future. Most critically, in this age, the micromation and wireless of QCM based HCHO sensors are inextricable and ineluctable topics. Nevertheless, with the rapid development of chemical theory, material synthesis technology, fabrication method, and electronic device miniaturization technology, micro wireless QCM based HCHO sensor will certainly be developed in the future, as shown in Fig. 16.

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