Effects of F doping on TiO₂ acidic sites and their application in QCM based gas sensors

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ABSTRACT

Titanium dioxide (TiO₂) and fluorine doped titanium dioxide (F-TiO₂) particles were prepared by a one-pot hydrothermal synthesis, and applied on quartz crystal microbalance (QCM) resonators to detect trace levels of nerve agent stimulant, dimethyl methylphosphonate (DMMP). DMMP sensing measurements exhibited that TiO₂ functionalized QCM resonators had fast response and recovery as well as satisfactory sensitivity. F-TiO₂ functionalized QCM resonators showed even faster response and higher sensitivity but rather slow recovery. The sensing mechanism and the effect of fluorine doping were examined by diffuse reflectance infrared Fourier transform spectroscopy, revealing that the adsorption took place at Brønsted acid sites at the initial stage and at Lewis acid sites later. Fluorine doping on TiO₂ greatly enhanced the acidity of Lewis acid sites, resulting in faster response but slower recovery than pure TiO₂. X-ray diffraction analyses demonstrated that the fluorine doping could enhance the crystallinity of anatase.

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1. Introduction

Highly active, volatile chemical warfare agents (CWAs) such as sarin and soman can cause rapid and severe inhibition of serine proteases. This inhibition is often fatal, as shown by the sarin attacks in the Tokyo subway in 1995 and the anthrax mailing incident in the USA in 2001. Thus, it is of great importance to detect a trace of CWAs and give a timely alarm for the public.

A wide range of transducer technologies, including semiconductor sensor [1,2] and mass sensor (quartz crystal microbalance [3,4], surface acoustic wave [5] microcantilever [6]), as well as newly developed fabrication technologies, such as metal-insulator-metal ensemble (MIME) [7] and microelectromechanical system (MEMS) [7,8] have been applied to meet these challenges. Of all these technologies, mass sensors are one of the most attractive technologies for their high sensitivity and fast response. Though the sensitivity of quartz crystal microbalance (QCM) based mass sensors are two or three orders magnitude lower than some other gravimetric devices such as surface acoustic wave and microcantilever, they still attract broad attention as they have many advantages such as low cost, easy to make and robust in practical applications. Until now, sensing materials used in related mass sensors have concentrated on

hydrogen-bond acidic branched copolymers [9,10]. Despite their high sensitivity, applications of these materials have been limited by their poor stability and relative long response and recovery time.

Titanium dioxide has received special attention because of its wide applications as photocatalysts [11], electrodes for lithium secondary batteries [12], and functional coatings in self-cleaning, antifogging [13,14], and chemical sensing [15]. It is also an acidic metal oxide with abundant Lewis and Brønsted acid sites. Considering the possibility that these acid sites may play a similar role as hydroxyl groups in hydrogen-bond acidic branched copolymers, it would be a meaningful attempt to detect CWAs by using TiO₂ instead of the copolymers. The completely new concept might, in turn, make the best use of the advantages of metal oxides, such as long-term stability and fast response in combination with high sensitivity of QCM.

The sensing capability of QCM sensors is generally based on the adsorption of target molecules. The modification of TiO₂ surface can affect its surface and interfacial properties, and thus may change its sensing characteristics. Surface fluorine doped TiO₂ (F-TiO₂) can be obtained in a simple ligand exchange way as follows: [16]

Previous reports on fluorine doped TiO₂ mainly concentrated on the adjustment of energy bands of TiO₂ in order to improve photocatalytic activities [17–19]. The strong electron withdrawing ability of fluorine makes the surface $\equiv\text{Ti}-\text{F}$ serve as an electron-

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trapping site, and thus enhances the acidity of Lewis acid sites of TiO_2 . This enhancement would facilitate the adsorption of CWAs as mentioned above.

In the current work, TiO_2 and pinecone like F- TiO_2 particles were synthesized by a facile hydrothermal method, and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Because of health hazards involved with nerve agents, surrogate dimethyl methylphosphonate (DMMP) is commonly used as simulant and was chosen for sensing experiments reported here. The adsorption of DMMP on TiO_2 and F- TiO_2 particles were investigated through diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Sensing characteristics of TiO_2 and F- TiO_2 functionalized QCM resonators to DMMP were also investigated, and the DMMP sensing mechanisms were discussed based on the results obtained by DRIFTS.

2. Experimental

2.1. Materials syntheses

TiO_2 and F- TiO_2 particles were synthesized by a facile one-pot hydrothermal method without and with addition of HF. In a typical procedure, 0.54 g of urea was first dissolved in 30 mL of ethanol in a 40 mL Teflon-lined autoclave. Then, 1.14 mL of HCl and 1.02 mL of tetrabutyl orthotitanate (TBOT) were sequentially injected using pipette into the above urea solution slowly under vigorous stirring. The molar ratio of TBOT: urea: HCl: ethanol in the resultant solution was 0.003: 0.009: 0.014: 0.772. After stirring for 30 min at room temperature, the autoclave was transferred into an electrothermic oven, heated up to 180 °C from room temperature and maintained at 180 °C for 4 h. A white precipitate was collected by washing twice with ethanol and centrifugal separation. Yellowish F- TiO_2 was synthesized by addition of 0.1 mL HF (0.0025 mol) under otherwise identical conditions. All materials synthesized in this work were calcined at 400 °C for 2 h before use.

2.2. Sensor fabrication

A drop-coating method was applied to coat both sides of a silver-coated (5 mm in diameter) piezoelectric quartz crystal (AT-cut, 9 MHz) with a sensing material. In a typical procedure, a sensing material (TiO_2 or F- TiO_2) was dispersed in water, and the obtained suspension was dropped onto the surface of silver electrode using a microsyringe. The QCM resonators with thin films were quickly dried at 30 °C in vacuum. Although it is a simple method, it was proved both effective and satisfactory for the aim of the current work [20].

2.3. Instrumentation

Functionalized QCM resonators were tested in a glass chamber which was put in an incubator where a controlled temperature was provided. A dynamic gas-mixing apparatus was used to steadily generate gas containing DMMP of low concentration. Vapor generated by liquid DMMP was taken away by a mass flow controller manipulated gas flow, and then was further diluted in proportion by another steady gas flow. In order to simulate the real environment and keep all environmental conditions consistent, all gas flows were dry air provided by an air compressor through desiccating columns. The relative humidity of dry air was strictly controlled at 5%. A four-way valve was applied to switch between dry air flow and diluted DMMP flow. Frequency shifts were recorded by a Protek c3100 universal counter linked to a computer.

Selectivity characterization was conducted under the same conditions except for the substitution of DMMP with H_2O and alcohols.

In situ DRIFTS was performed on a Nexus 670 (Thermo Nicolet) FT-IR spectrometer equipped with an in situ diffuse reflection chamber and a high-sensitivity MCT detector. Materials for in situ DRIFTS studies were placed in a ceramic crucible in the in situ chamber. Mass flow controllers were used to control flow rates, which were identical to the gas sensing tests. Prior to recording each DRIFTS spectrum, the materials were pretreated with N_2 at 80 °C for 1 h, and then cooled to room temperature. After acquiring a reference spectrum, a flow of 500 mL/min N_2 was introduced into a gas mixing apparatus to carry away DMMP vapor, and the mixed gas was let into the in situ diffuse reflection chamber. A series of DMMP adsorption spectra were obtained with time. The measurements lasted for 30 min. All spectra reported here were collected at a resolution of 4 cm^{-1} for 100 scans.

A temperature-programmed desorption (TPD) procedure was used to study the adsorption intensity of DMMP on the surface of F- TiO_2 . The powders were sieved to 20–40 mesh before pre-saturated with DMMP at 30 °C. Subsequently, the samples were purged in Ar at 30 °C for 120 min, and then the furnace was ramped at 10 °C/min to 500 °C. A mass spectrometer (Hiden HPR 20) was used for on-line monitoring the signals of MMP^+ ($m/e = 93$), the fragment of DMMP.

XRD patterns of TiO_2 and F- TiO_2 were recorded on a Holand PANalytical X'Pert PRO MPD X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) operated at 40 kV and 40 mA. SEM observations were carried out on a Hitachi S-4300 field emission scanning electron microscope.

3. Results and discussion

3.1. Morphologies of TiO_2 and F- TiO_2 particles

Fig. 1 shows SEM images of as-synthesized TiO_2 and F- TiO_2 . Without addition of HF, obtained TiO_2 particles were irregular and agglomerated. With addition of HF, however, pinecone-like F- TiO_2 particles were obtained. The formation mechanism of the structure was discussed in our previous work [21], and is attributed to both HF etching and Ostwald ripening.

XRD analyses (Fig. 2) revealed that both TiO_2 and F- TiO_2 were anatase (JPCDS No. 89-4921). Compared with TiO_2 , the intensities of XRD peaks of F- TiO_2 became stronger, and their widths became narrower, indicating enhanced crystallinity. This is because F ions can induce crystallization of anatase [22,23].

3.2. Adsorption of DMMP on TiO_2 and F- TiO_2 particles

Understanding the interaction between a target and a sensing material is important for developing highly effective sensors. The interaction of DMMP with TiO_2 and F- TiO_2 surfaces was investigated by DRIFTS. Most previous works mainly focused on the dissociation processes occurring on TiO_2 surface [24–26]. However, the detailed DMMP adsorption mechanism on TiO_2 surface at room temperature and effects of fluorine doping have not been investigated, and reported with an eye to mass sensors. Herein, the adsorption mechanism of DMMP on TiO_2 and especially on F- TiO_2 were discussed in terms of DRIFTS measurements.

The DRIFTS spectra of adsorbed DMMP on TiO_2 and F- TiO_2 can be broken into two regions: one is the high-frequency region from 3700 to 2800 cm^{-1} that contains the methyl and hydroxyl stretching vibrations, and the other is the low-frequency region from 1800 to 1000 cm^{-1} that contains the C–O and P=O stretching vibrations and the methyl deformation vibrations. The region below 1000 cm^{-1} is rather complex and hard to distinguish, so it is not discussed in this work.

There are two kinds of DMMP adsorption on TiO_2 surface: nondissociative adsorption and dissociative adsorption. Scheme 1

Fig. 1. SEM images of (a) TiO_2 and (b) F-TiO_2 particles.

shows two modes of nondissociative adsorption. In Mode I, DMMP is adsorbed through the interaction of the oxygen of its P=O bond with isolated hydroxyl group (Brønsted acid site) on the surface of TiO_2 . In Mode II, the electron-rich oxygen of its P=O bond coordinates with Ti^{4+} , which is a Lewis acid site on the surface of TiO_2 . These two modes portray two possible nondissociative adsorption mechanisms involving Brønsted and Lewis acid sites, respectively. Scheme 2 shows the dissociative adsorption that involves the change of OCH_3 , which could be monitored by DRIFTS

Fig. 2. XRD patterns of TiO_2 and F-TiO_2 particles.

Scheme 1. Schematic illustration of the nondissociative adsorption modes of DMMP on the surface of TiO_2 .

Scheme 2. Schematic illustration of the dissociative adsorption mode of DMMP on the surface of TiO_2 .

Fig. 3. DRIFTS spectra of DMMP on TiO_2 particles at different times: (a) 1 min, (b) 2 min, (c) 3 min, (d) 5 min, (e) 10 min, (f) 15 min, (g) 30 min.

Table 1

A summary of band assignments for DMMP in gas phase and for DMMP adsorbed on TiO₂ and F-TiO₂ surfaces at 29 °C.

Gas phase	On TiO ₂	On F-TiO ₂	Assignments
3014	2999	2995	$\nu_a(\text{CH}_3\text{P})$
2962	2958	2956	$\nu_a(\text{CH}_3\text{O})$
2921	2927	2927	$\nu_s(\text{CH}_3\text{P})$
2859	2852	2852	$\nu_s(\text{CH}_3\text{O})$
		1730	$\nu(\text{C}=\text{O})$
1471	1464	1464	$\delta_a(\text{CH}_3\text{O})$
1423	1417	1419	$\delta_s(\text{CH}_3\text{P})$
1315	1313	1313	$\delta_s(\text{CH}_3\text{P})$
1276	1244		$\nu(\text{P}=\text{O})$
	1218		$\nu(\text{P}=\text{O})$
		1275	$\nu(\text{P}=\text{O})$
		1244	$\nu(\text{P}=\text{O})$
1188	1188	1188	$\rho(\text{CH}_3\text{P})$
1075	1060	1051	$\nu(\text{C}-\text{O})$
		1076	$\nu(\text{C}-\text{O})$

[26]. Such reaction occurs frequently in hydrolysis and photodegradation processes.

3.2.1. Interaction of DMMP with TiO₂

In the high-frequency region, molecular adsorption of DMMP is evidenced by the asymmetric and symmetric modes of CH₃(OCH₃) stretching vibrations at 2958 and 2852 cm⁻¹ (Fig. 3 and Table 1), which are almost the same as those of gaseous DMMP reported in literature [27] and do not change during the whole course. In addition, the bands at 2999 and 2927 cm⁻¹ are attributed to $\nu_a(\text{CH}_3\text{P})$ and $\nu_s(\text{CH}_3\text{P})$, respectively, which are also a proof of molecular adsorption of DMMP on TiO₂.

As shown in Scheme 1, both nondissociative adsorption modes only involve the P=O bond, and the adsorption of DMMP can thus be examined by the perturbation of P=O. In the low-frequency region, the P=O stretching mode, which occurs at 1276 cm⁻¹ for gaseous DMMP, shifts to 1218 cm⁻¹. Simultaneously, a broad negative band at 3710–3620 cm⁻¹ in the high-frequency region as well as a negative band at 1622 cm⁻¹ in the low-frequency region appear and increase with time, indicating consumption of strongly adsorbed water molecules [28]. The fact that the development of the 1218 cm⁻¹ stretching mode of P=O is accompanied by a decrease of strongly adsorbed water molecules is explained by hydrogen bonding of DMMP molecules to the surface through strongly adsorbed water molecules as illustrated in Mode I. With time going on, about 10 min later, a new band at 1244 cm⁻¹ becomes discernible and eventually overpasses the band at 1218 cm⁻¹ after 30 min adsorption. As no further decrease of strongly adsorbed water molecule peak was observed, the new band at 1244 cm⁻¹ could be attributed to the adsorption of DMMP

on Lewis acid sites as illustrated by Mode II in Scheme 1. The dissociative adsorption illustrated in Scheme 2 involves a formation of a bound methoxy species (Ti-OCH₃) that has a $\nu(\text{Ti}-\text{OCH}_3)$ stretching band at 2831 cm⁻¹ according to literature [29]. However, no band at 2831 cm⁻¹ was observed at all measurement times, meaning no dissociative adsorption had occurred on the surface of TiO₂. In fact, an on-line mass spectroscopy was also applied to detect any possible dissociation products such as CH₃OH, and no signals of such products were recorded. The results reveal that the adsorption of DMMP on TiO₂ is nondissociative adsorption rather than dissociative adsorption, and the adsorption is through hydrogen bonding at the initial stage but through coordination to the Lewis acid sites later. The hydrogen bonding adsorption mode may be referred as dynamically controlled because of its low active energy, and the Lewis acid sites adsorption mode may be referred as thermodynamically controlled because of its high stability. The adsorption on Lewis acid sites via coordination is more stable than that through hydrogen bonding, which means the former is more difficult to desorb from TiO₂ surface than the latter.

3.2.2. Interaction of DMMP with F-TiO₂

Fig. 4 shows DRIFTS spectra of DMMP adsorbed on F-TiO₂ at 30 °C. In the high-frequency region, similar methyl stretching vibrations were observed at 2956 and 2852 cm⁻¹ for OCH₃, 2995 cm⁻¹ for $\nu_a(\text{CH}_3\text{P})$ and 2927 cm⁻¹ for $\nu_s(\text{CH}_3\text{P})$. However, the low-frequency region is different. F-TiO₂ is highly dehydroxylated as a result of ligand substitution. As a result, no characteristic peaks of hydrogen bonding adsorption were observed as mentioned in DMMP adsorption on TiO₂. Instead, a peak at 1275 cm⁻¹ appeared at beginning of DMMP exposure, and increased gradually. Compared with the IR spectrum of gas phase DMMP, the peak could be assigned to the stretching mode of P=O of gaseous DMMP. After 5 min exposure, a band centered at 1255 cm⁻¹ becomes discernible and overpasses the peak at 1275 cm⁻¹ quickly. In combination with the results obtained for TiO₂, we refer it as the adsorption of DMMP on Lewis acid sites. A careful comparison with the position of P=O on TiO₂ indicates that a blue shift occurred for F-TiO₂. Similar phenomenon was reported previously in the work of Österlund and coworkers [30]. They found the $\nu(\text{P}=\text{O})$ bond in diisopropyl fluorophosphate (DFP) has a higher frequency than in DMMP, and they ascribed it to the electron withdrawing of electronegative halogens bonded to the phosphorus atom. In the current work, although the fluorine atom is bonded to Ti⁴⁺ rather than phosphorus atom, the electron withdrawing effect still can act through titanium atom. As a result, the frequency of $\nu(\text{P}=\text{O})$ shifts to 1255 cm⁻¹, 11 cm⁻¹ higher than that on TiO₂. The shift indicates that the existence of fluorine atoms on TiO₂ surface can enhance the acidity of the Lewis acid sites. This enhancement results in a stronger adsorp-

Fig. 4. DRIFTS spectra of DMMP on F-TiO₂ particles at different times: (a) 1 min, (b) 2 min, (c) 3 min, (d) 5 min, (e) 10 min, (f) 15 min, (g) 30 min.

tion of DMMP on F-TiO₂ than on pure TiO₂, making desorption of DMMP from the adsorption sites even harder. Thus, the adsorption of DMMP on F-TiO₂ is not exactly the same as that on TiO₂.

Significant differences in DRIFTS spectrum were noted between TiO₂ and F-TiO₂ particles. New bands centered at 1730 cm⁻¹, 1686 cm⁻¹ and 1535 cm⁻¹ were observed simultaneously with the Lewis acid site adsorption on F-TiO₂, but not observed on TiO₂. Although previous works [24,25,31] mentioned some similar bands in context with DMMP dissociation and photocatalytic oxidation, those results do not meet the circumstance in the current work and the bands are not well fitted. Since no illumination was applied in the current work, the most possible reaction occurred would be the decomposition of DMMP on F-TiO₂. The direct evidence is the broad peak around 3200 cm⁻¹, which can be attributed to $\nu(\text{O-H})$ of the surface-bound decomposition product of CH₃OH. Such surface-bound CH₃OH is probably active enough to react in two pathways. One is that they may be oxidized as evidenced by the appearance of the peak at 1730 cm⁻¹, which is the $\nu(\text{C=O})$ of the surface-bound formaldehyde [26]. The formed surface-bound formaldehyde may be further oxidized. In fact, the broad band around 1535 cm⁻¹ suggests the formation of formate or carboxylate on F-TiO₂. The other is an aldol condensation-type reaction between adsorbed DMMP and methoxy groups according to Kiselev et al.'s work [30], which is supported by the peak at 1686 cm⁻¹. However, both pathways must be minority reactions as evidenced by the weak intensity of the peaks. It is understood that all the reactions occurred on the surface and all products were hard to leave because of the strong adsorption of Lewis acid sites, which could inhibit further adsorption and reaction on the surface. Therefore, the DMMP adsorption on F-TiO₂ is quite different from that on TiO₂. Firstly, F-TiO₂ is highly dehydroxylated, and adsorption only occurs on Lewis acid sites. Secondly, the existence of fluorine atoms enhances the acidity of Lewis acid sites, resulting in a stronger adsorption and harder desorption. The existence of fluorine may also activate the adsorbed DMMP, making them partially decompose.

Compared with the results obtain by Tripp and his coworkers, though there are some similarities for pure TiO₂ in DMMP sorption at room temperature, the main difference comes from the effects of F doping. On one hand, the F doping changed the DMMP adsorption mode, and on the other hand, the existence of F lowered the decomposition temperature of DMMP.

3.3. DMMP responses of TiO₂ and F-TiO₂ functionalized QCM resonators

The identification of TiO₂ and F-TiO₂ surface acid sites and the interaction between surface acid sites and DMMP would doubtlessly enhance the understanding of response mechanism in DMMP sensing measurements. Based on DRIFTS results mentioned above, the Lewis and Brønsted acid sites on the surface of the two sensing materials would play a major role in inducing the frequency change of functionalized QCM resonators.

Typical response profiles of TiO₂ and F-TiO₂ functionalized QCM resonators exposed to 10 ppm of DMMP at 15 °C are depicted in Fig. 5. TiO₂ shows a quite reasonable response to DMMP under current conditions (Fig. 5a). The sensitivity, the ratio of frequency shift (Hz) to DMMP concentration (ppm) is 5 Hz/ppm. However, the response and recovery time are 27 s and 31 s, respectively, much faster than commonly used hydrogen-bond acidic branched copolymers. The later always show response and recovery time as long as several minutes. Surprisingly, the F-TiO₂ functionalized QCM resonator exhibits an even higher sensitivity as well as faster response than pure TiO₂ (Fig. 5b). The sensitivity reaches as high as 16 Hz/ppm, and the response time shortens to only 8 s. However, the recovery time is quite long, and the adsorption seems irreversible. Although it is hard to recover under measurement con-

Fig. 5. Response profiles of TiO₂ (a) and F-TiO₂ (b) functionalized QCM resonators to DMMP at 15 °C. The DMMP concentration was 10 ppm.

ditions, the QCM resonator could be recovered by being placed in a vacuum oven at 80 °C for 2 h.

Variation of the responses of TiO₂ and F-TiO₂ functionalized QCM resonators with DMMP concentration are shown in Fig. 6. Both resonators exhibit a good linear relationship of response vs. concentration at low DMMP concentrations (4–30 ppm). The slope of the curves, i.e., the sensitivity of the resonators, is 5 Hz/ppm for TiO₂ and 16 Hz/ppm for F-TiO₂, respectively. The sensitivity of F-TiO₂ functionalized resonator is even higher than some commonly used hydrogen-bond acidic branched copolymers [32,33], which may make it possible to detect DMMP even at ppb levels.

To examine the recovery ability of F-TiO₂ functionalized resonators, DMMP response measurements were conducted at varied

Fig. 6. Variation of the responses of TiO₂ and F-TiO₂ functionalized QCM resonators with DMMP concentration at 15 °C.

Fig. 7. Response profiles of F-TiO₂ functionalized QCM resonators to DMMP at varied temperatures. The DMMP concentration was 10 ppm.

temperatures as shown in Fig. 7. Compared with the TiO₂ functionalized QCM resonator which could easily recover at even as low as 10 °C after switching from DMMP to fresh air, F-TiO₂ could only partially recover. With increase of temperature, recovery improved but still could not fully recover even at 25 °C. The thermal stability of DMMP adsorbed on the surface of F-TiO₂ was explored by means of temperature-programmed desorption (TPD) in flowing Ar, and the result is shown in Fig. 8. Similar with the sensing results, most of the adsorbed DMMP molecules could desorb from the surface at 30 °C. However, it took quite a long time (more than 2 h). When the temperature increased to 85 °C, another small desorption peak appeared. It could be attributed to the dissociation of DMMP which had not desorbed from the surface of F-TiO₂ at room temperature. The relatively low dissociation temperature compared with pure TiO₂ (>200 °C) [26] again proved the effect of F doping as discussed in Section 3.2. The enhanced acidity made DMMP easier to dissociate compared with pure TiO₂.

The difference in sensing properties of TiO₂ and F-TiO₂ functionalized QCM resonators can be explained by different effective acid sites on surface as revealed by DRIFTS. As discussed above, DMMP adsorbs on pure TiO₂ through hydrogen bonding at the initial stage and through coordination to Lewis acid sites later. It is currently hard to discern which plays a predominant role in the whole sensing process, but both interactions are clearly not too strong for DMMP to desorb from the surface of TiO₂ by flushing with fresh air at room temperature. Although the interaction sites are also Lewis acid sites for F-TiO₂, F-TiO₂ functionalized QCM resonator exhibits higher sensitivity, shorter response time but partial irreversibility at room temperature. Such different response characteristics can be attributed to the change of acidity of Lewis acid sites resulting from fluorine doping, as revealed by DRIFTS. Because

Fig. 8. DMMP desorption during Ar-TPD of F-TiO₂.

Fig. 9. Responses of the QCM sensor to DMMP and interfering vapors at saturated concentrations.

of the electron withdrawing ability of fluorine, F-TiO₂ shows even higher Lewis acidity than pure TiO₂. This enhancement of acidity makes Lewis acid sites of F-TiO₂ more accessible for DMMP, thus resulting in faster response. However, this enhancement also makes the adsorption stronger so that DMMP is more difficult to desorb from the sites, exhibiting partial irreversibility.

Selectivity is a key property for sensors. However, in only a few instances has the selectivity of detection been investigated. In this section, the selectivity of TiO₂ and F-TiO₂ to DMMP were studied in consideration of possible interfering agents such as H₂O and alcohols. Each organic vapor was at a saturated concentration. As can be seen in Fig. 9, the selectivity of pure TiO₂ was quite poor. The responses of TiO₂ functionalized QCM resonators to H₂O, methanol and ethanol were much higher than to DMMP. In contrast, F-TiO₂ functionalized QCM resonators exhibited excellent selectivity. Though the concentration of interfering agents was much higher than DMMP, the response of F-TiO₂ was only 42, 40, 28 Hz to H₂O, methanol and ethanol, respectively, far lower than to DMMP (172 Hz). Undoubtedly, the difference could be attributed to the effect of F doping. Considering the effects of hydrophobic treatment of coating surfaces with perfluorooctyltriethoxysilane (POTS) [34,35], it is not difficult to understand the excellent selectivity of F-TiO₂. The existence of F on the surface of TiO₂ can prohibit the adsorption of polar molecules such as H₂O and alcohols, resulting in quite low responses to them.

4. Conclusion

TiO₂ and F-TiO₂ particles were prepared by a facile one-pot hydrothermal synthesis and used as sensing material for QCM gas sensors to detect a trace level of CWAs surrogate DMMP. Compared with traditional DMMP sensing materials used for mass sensors, i.e., hydrogen bond acidic branched copolymers, acidic metal oxide TiO₂ can greatly improve the gas sensing characteristics to much shorter response (27 s) and recovery (31 s) time. F-TiO₂ can further improve the gas sensing characteristics by shortening the response time to only 8 s but at the price of partial irreversibility. F-TiO₂ showed excellent selectivity in respect of interfering gases such as H₂O and alcohols, which is another great improvement of the sensing characteristics of QCM based sensors. Both of them can be used as sensing material on mass sensors to detect DMMP for different requirement. Mechanism studies show that the adsorption of DMMP on TiO₂ takes place at Brønsted acid sites at the initial stage and at Lewis acid sites later. However, F-TiO₂ shows different characteristics because of high dehydroxylation. The adsorption of DMMP only occurs at Lewis acid sites. It is rather stronger on F-TiO₂ than on pure TiO₂ because of the strong electron withdrawing ability of fluorine. The key importance of the current work is not

only the first time to detect DMMP by using TiO₂ and F-TiO₂ functionalized QCM resonators, but also the enhanced understanding of different adsorption behaviors of the two sensing materials caused by fluorine doping, which provides a new method to improve the selectivity of TiO₂ for detection of DMMP.

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