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MOLECULARLY IMPRINTED TIO_2 INORGANIC FILM AND PVDF/TIO_2 COMPOSITE FILM AS SENSORS FOR THE DETECTION OF CHEMICAL THREAT AGENTS USING QUARTZ CRYSTAL MICROBALANCE

(TiO_2 Filem Tak Organik dan Filem Komposit PVDF/TiO_2 Molekul Tercetak sebagai Sensor untuk Mengesan Agen Kimia Berbahaya Menggunakan Penimbang Mikro Kristal Kuarza)

Xuan Hao Lin[1], Kah Sing Chooi[1], Sam Fong Yau Li[1, 2]*

[1]*Department of Chemistry,*
National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[2]*NUS Environmental Research Institute (NERI),*
#02-01, T-Lab Building (TL), 5A Engineering Drive 1, Singapore 117411, Singapore

**Corresponding author: chmlifys@nus.edu.sg*

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Abstract

In this paper, we report molecularly imprinted TiO_2 inorganic film ($MITiO_2$) and PVDF/TiO_2 composite film ($MIPTiO_2$) as sensors for the detection of parathion methyl (PTM), a simulant of chemical threat agent (CTA) using quartz crystal microbalance (QCM). PTM was used as a molecular template for the imprinting of the sensor film. The $MITiO_2$ showed a greater response (Δf 19 Hz) to 9.88 μM of PTM than that (Δf 2 Hz) of the $MIPTiO_2$. The ratios of TiO_2/template and PVDF/TiO_2/template were optimized. Time for the UV degradation of the template was also optimized. $MITiO_2$ sensor shows good potential for the detection of CTA, other chemical and biochemical pollutants.

Keywords: molecularly imprinted polymer, quartz crystal microbalance, sensor, TiO_2, parathion methyl

Abstrak

Dalam kajian ini, kami melaporkan TiO_2 filem tak organik ($MITiO_2$) dan filem komposit PVDF/TiO_2 ($MIPTiO_2$) molekul tercetak sebagai sensor untuk mengesan paration metil (PTM), yang merupakan ejen bahan kimia berbahaya (CTA) menggunakan penimbang mikro kristal kuarza (QCM). PTM telah digunakan sebagai templat molekul untuk peneraan filem sensor. $MITiO_2$ menunjukkan tindak balas yang lebih besar (Δf = 19 Hz) pada kepekatan 9.88 μM daripada PTM berbanding $MIPTiO_2$ (Δf = 2 Hz). Nisbah TiO_2/templat dan PVDF/TiO_2/templat telah dioptimumkan. Masa untuk degradasi UV bagi templat juga telah dioptimumkan. Sensor $MITiO_2$ menunjukkan potensi yang baik untuk mengesan CTA, serta bahan kimia yang lain dan bahan pencemar biokimia.

Kata kunci: polimer molekul tercetak, penimbang mikro kristal kuarza, sensor, TiO_2, paration metil

Introduction

Chemical threat agents (CTA) are toxic synthetic chemicals that can be dispersed in various forms like gas, liquid, aerosol or adsorbed to solid particles [1]. CTA were deployed in war to kill or incapacitate the enemy. Nerve agents are among the most potent of all reported CTA. Nerve agents like Sarin, Tabun and Soman act as inhibitor irreversibly binding to the enzyme acetylcholinestearase, an enzyme that normally destroys and stops acetylcholine, a neurotransmitter. Inhibition of the enzyme would lead to an accumulation of acetylcholine, producing a perpetual

excited state in the nerve (e.g. constant muscle contraction) [2]. The critical effects of this would be the paralysis of the respiratory muscles and inhibition of the respiratory centre in the central nervous system, leading to death of the victim by asphyxiation within minutes [3]. Due to their high toxicity, imperceptibility to senses and rapid action, administration of antidote to victims exposed to such chemicals were often carried out too late. In addition, these CTAs are potential weapons of choice for terrorist organizations that could threaten national security [4]. Thus, there is a need for a highly sensitive and selective sensor to be developed for the detection of such CTAs as a preventive measure.

Various analytical methods had been used in the military and civil agencies for the detection of CTA such as liquid chromatography and gas chromatography [5, 6]. Although these methods are advantageous in terms of having a low limit of detection, they are usually not selective. One selective new method is based on molecular imprinting polymers (MIPs). MIP polymers are synthesized when monomers are polymerized in the presence of template molecules (Figure 1). The functional groups in the monomers would orient toward their counteracting functional groups in the template via forces of interactions like hydrogen bonding, van der Waals interaction and dipole-dipole interactions etc. [7]. Subsequent cross-linking of the polymer would hold the template molecule in place. Upon removal of the template molecules, the remaining cavities that retained the molecular configuration of the template would act as highly specific molecular recognition sites [8].

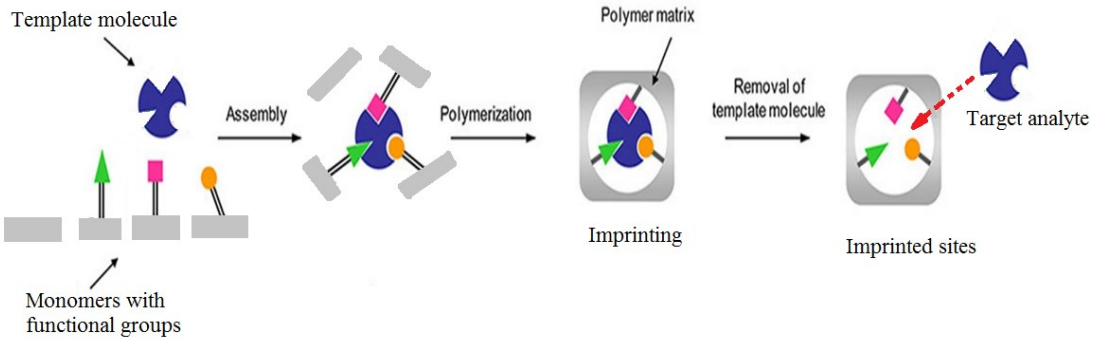

Figure 1. Illustrative formation of molecularly imprinted polymer sensor

A MIP sensor on gold coated AT cut quartz could be coupled with mass sensitive devices such as QCM for the detection of target analyte molecules. A QCM flow cell consists of two electrodes where the MIP sensor sits in between. Resonance frequency of the quartz based sensor with applied voltage is sensitive to mass change. Binding of target analyte molecules onto the molecular cavities on the MIP would lead to an increase in mass which is reflected by a proportional drop in its resonance frequency [9,10,11]. The relationship between change of resonance frequency and change of mass for a QCM sensor could be described by the Sauerbrey equation (eq. 1):

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m \quad (1)$$

where Δf is the frequency change (Hz), f_0 is the resonant frequency (Hz), Δm is the mass change (g), A is the coated area (cm^2), ρ_q is the density of quartz (g/cm^3), μ_q is the shear modulus of quartz ($g/cm\ s^2$).

Hydrophobic PVDF (-(CH_2CF_2)-) has high affinity to hydrophobic analyte molecules. The polarity of PVDF enables dipole-dipole interaction in addition of Van der Waals interaction with the template molecule. These characteristics, in addition to its chemical and thermal stability, enable PVDF a suitable candidate as the polymer of MIP. PVDF has high affinity to hydrophobic molecules but low affinity to hydrophilic molecules. Therefore, it will be good to include some hydrophilic materials into PVDF so that the final composite sensor could be optimized to bind to both hydrophobic and hydrophilic molecules. TiO_2 particles with enriched surface hydroxyl groups could

bind to hydrophilic molecules. In addition, with UV irradiation it could photocatalytically degrade template and analyte molecules which facilitate the template removal and cleaning after analysis. TiO_2 particles could be prepared from titanium butoxide ($Ti(OBu)_4$). Upon exposure to moisture, $Ti(OBu)_4$ rapidly undergoes hydrolysis to form TiO_2 nano crystals. When $Ti(OBu)_4$ was used alone the rapid formation of the TiO_2 particles neighboured the template molecules enabled specific recognition sites to be formed on the MIP [12]. PTM, commonly found in pesticides, was chosen as the template due to its lower toxicity than real CTAs and structure similarity to organophosphorous CTAs like sarin (Figure 2).

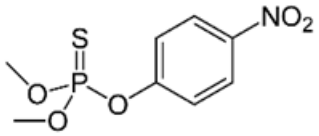

Figure 2. Molecular structure of parathion methyl

Template removal to form MIP is one of the critical and difficult steps. Extra chemicals introduced for template removal may destroy the newly formed molecular cavities. Without extra chemicals introduced, photodegradation have advantages in keeping the molecular cavities not touched with other chemicals during template removal. PTM has been reported to undergo photolysis in the presence of sunlight or more specifically, ultraviolet (UV) light [13]. In addition, metal oxides like titanium dioxide (TiO_2) that exhibits high photocatalytic activity have been shown to be able to decompose CTA simulants completely into inorganic products under UV light [14]. Upon absorption of UV light, positively charged holes and negatively charged electrons are generated and these two species can then initiate redox reactions via the generation of reactive species like hydroxyl radicals and superoxides [15]. Therefore, either alone or together with PVDF, photocatalytically active TiO_2 could assist the template removal during MIP preparation and sensor post-cleaning after analysis. Here we report molecularly imprinted TiO_2 inorganic film and PVDF/TiO_2 composite film as sensors for the detection of PTM using QCM. Removal of template molecules was completed through their photocatalytic degradation by the surrounding TiO_2 particles under UV irradiation.

Materials and Methods

Materials

Polyvinylidene difluoride powder (M.P. 155 – 160 °C) was from Alfa Aesar (Ward Hill, MA). Titanium(IV) butoxide ($Ti(OBu)_4$, reagent grade 97%) was from Sigma Aldrich (St. Louis, MO, USA). Parathion-methyl ($C_{10}H_{14}NO_5PS$, 99.5%) was from Chem Service Inc. (West Chester, PA, USA). N,N-dimethylformamide (C_3H_7NO, reagent grade 99.5%) was from Merck (Darmstadt, FR, Germany). Tetrahydrofuran (C_4H_8O, reagent grade 99.7%) was from VWR International (Singapore). TiO_2 nanoparticles (12 nm) were synthesized according our previously reported sol-gel method from the hydrolysis of $TiOSO_4$ in an alcohol and water mixture [16].

Preparation of molecularly imprinted PVDF/TiO_2 composite sensor (MIPTiO_2)

A certain quantity of PVDF powder and PTM were dissolved in DMF. And then TiO_2 particles were dispersed into the transparent PVDF/PTM/DMF solution with 10 minutes of sonication. Mass ratios of PVDF, TiO_2 nanoparticles and PTM in the ad-mixture were 5:5:1, 2:2:1 and 1:1:1 respectively for different sensors. 20 µL of the ad-mixture was applied onto the gold coated surface of the AT cut quartz crystal chip. After dry at room temperature, the chip was wetted by 700 ppm of potassium bromate aqueous solution and irradiated with monochromatic 365 nm UV light (100 W, mercury lamp, 18 mW/cm^2) for a certain period of time for the template degradation. The photocatalytic degradation of parathion methyl was reported before [17, 18]. After template removal the sensor was rinsed with DI water for several times before use.

Preparation of molecularly imprinted TiO_2 film sensor (MITiO_2)

$Ti(OBu)_4$ was used for the preparation of MITiO_2. Due to $Ti(OBu)_4$ sensitive to moisture in air, it was necessary to avoid prolonged exposure of $Ti(OBu)_4$ to the air during the preparation procedures. The reaction vials to be used were first blown with nitrogen gas for 3 minutes to dispel adsorbed moisture on the wall. Then a certain quantity of

$Ti(OBu)_4$ was added into one of the vials and rapidly capped to avoid substantial entry of moisture. THF was then added to the $Ti(OBu)_4$ and the vial was sonicated for 5 minutes to obtain a homogenous solution. Similar procedure was applied when preparing a PTM/THF solution. Then PTM/THF solution was added into $Ti(OBu)_4$/THF solution and mixed well. Subsequently, the mixture was topped up with THF such that the ratio of the total mass (g) of TiO_2 and PTM to volume (mL) of THF was 3/1000. Different molar ratios of TiO_2/PTM 10:1, 5:1, 2:1 and 1:1 were used to prepare different sensors. The final solution mixture was further sonicated for 5 minutes. 20 µL of the ad-mixture was placed onto the gold surface of quartz chip. When exposure to air, $Ti(OBu)_4$ hydrolyzed to form TiO_2 nanocrystallines wrapping PTM template molecules. $Ti(OBu)_4$ hydrolysis process was completed at room temperature after overnight. After complete hydrolysis, the chip was wetted by DI water and irradiated with monochromatic 365 nm UV light (100 W, mercury lamp, 18 mW/cm^2) for a certain period of time for the template degradation. Once template molecules were removed, the sensor was rinsed with DI water for a few times and then was ready for use.

Preparation of non-imprinted polymers (NIP)

NIPs of PVDF/TiO_2 composite and pure TiO_2 were prepared using similar procedures but without including template PTM molecules. They were named as PVDF/TiO_2 NIP and TiO_2 NIP, respectively.

Evaluation of sensors

Evaluation of the sensors were conducted using a Q-Sense E4 QCM Analyzer (Biolin Scientific) consisting of a QE 401 Electronics Unit, a QCP 401 Chamber Platform and 4 QFM 401 Flow Modules. The MIPTiO_2 and MITiO_2 sensor chips were mounted onto the flow modules and fitted onto the platform in the temperature-controlled chamber with the liquid inlet and outlet tubes connected. The resonance frequencies of the sensor chips were first measured to ensure that with the thickness of the MIP films their resonance frequencies were still within the detection range of QCM. With the chamber's temperature maintained at room temperature (25°C), the liquid flow was started. Deionized water was first introduced into the flow module at 50 µL/min for 5 minutes before increasing to 100 µL/min. Measurement of the frequency change was then started. DI water flow was continued until the frequency has stabilized before PTM analyte solution was introduced. The flow of analyte solution was continued from for about 1.5 hours until the resonance frequency has stabilized before switching to DI water rinsing for 30 minutes. The frequency change was taken at the 70th minute after analyte introduction.

Results and Discussion

Template removal

When TiO_2 is activated by UV light, holes (h^+) are formed in the valence band and electrons (e^-) in the conduction band of TiO_2. Photogenerated holes and electrons further react with water and oxygen to produce hydroxyl and superoxide radicals. The photocatalytic degradation of PTM was reported before [17, 18]. PTM reacted with hydroxyl radicals to produce paraoxon methyl, which further reacted with hydroxyl radicals to generate p-nitrophenol, hydroquinone, carboxylic acids and other intermediates to final CO_2 gas and phosphate ions. To enhance photocatalytic degradation of PTM, electron acceptor bromate was added as an additive. Electron acceptors like BrO_3^- ions removed photogenerated electrons from the conduction band resulting in better electron-hole separation and so photocatalytic efficiency (equation 2) [15]:

$$BrO_3^- + 2H^+ + 2e^- \rightarrow BrO_2\cdot + H_2O \quad (2)$$

Based on previous reports, TiO_2 UV photocatalytic degradation of organophosphorous compounds like PTM and diethylphosphoramidate was carried out in the presence of suspended TiO_2 particles in an aqueous solution and the time taken for complete photodegradation of these molecules required at least a few hours [14, 18].

Non-imprinted polymers (NIP)

PVDF/TiO_2 NIP and TiO_2 NIP showed some baseline response to 9.88 µM of PTM solution. Mass ratio 1/1 of PVDF/TiO_2 was used for the PVDF/TiO_2 NIP. Their resonance frequency changes are listed in Table 1. TiO_2 NIP had a frequency change of 4.0 Hz, which was lower than that (8.0 Hz) of PVDF/TiO_2 NIP although both were low enough as background baseline. Lower NIP response was preferred because lower baseline could enhance detection sensitivity.

Table 1. Response of PVDF/TiO_2 NIP and TiO_2 NIP to 9.88 µM of PTM solution

Name of NIPs	Frequency Changes Δf (Hz)
PVDF/TiO_2*	8.0
TiO_2	4.0

* Mass ratio of PVDF to TiO_2 was 1/1

MIPTiO_2 sensor

Figure 3 shows the changes of resonance frequency (Δf) of MIPTiO_2 sensors with different ratios of PVDF/TiO_2/PTM responding to 9.88 µM of PTM aqueous solution before and after template removal. Before template removal MIPTiO_2 sensor with 1/1/1 ratio of PVDF/TiO_2/PTM in the preparation as-mixture had higher response to PTM than the other two sensors with lower PTM percentage, which could be due to the interactions between template PTM molecules and analyte PTM molecules. However, after template removal by UV irradiation, responses of all the three sensors greatly decreased which could be attributed to two reasons. The first reason was that after UV irradiation, TiO_2 may exhibit both natural and permanent superhydrophilicity [19 – 21]. Natural superhydrophilicity was reversible and mainly induced by heating effect of UV light, which dispelled some moisture molecules from TiO_2 surface and then the leftover hydrogen bonded moisture molecules spread out thermodynamically to compensate the decrease of surface tension due to the partial loss of water molecules. Permanent superhydrophilicity based on natural superhydrophilicity was mainly attributed to the stabilization layer such as outer SiO_2 layer [21] or the PVDF layer in our case to stabilize surface hydroxyl groups. The second reason could be attributed to the appearance of some hydrophilic functional groups on the surface of PVDF after UV irradiation with the existence of TiO_2 [22, 23]. Therefore, after template removal by UV irradiation, the sensor surface was highly likely very hydrophilic and so have very weak interaction with hydrophobic PTM molecules, resulting in low response to PTM.

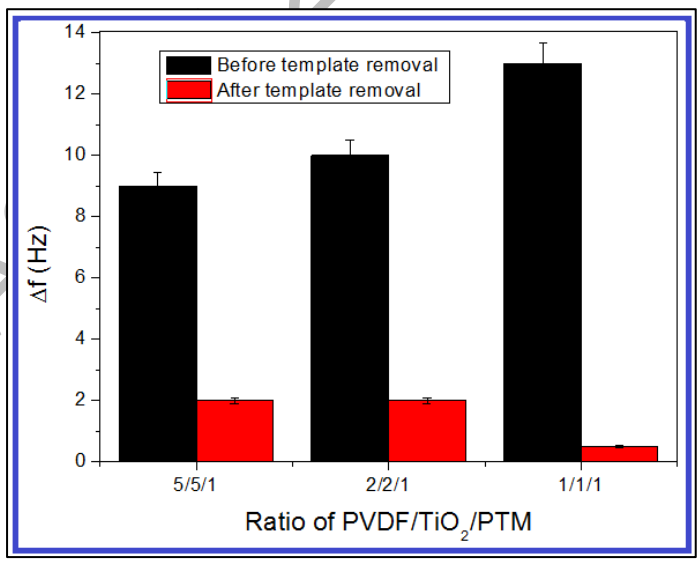

Figure 3. Changes of resonance frequency (Δf) of MIPTiO_2 sensors with different ratios of PVDF/TiO_2/PTM responding to 9.88 µM of PTM aqueous solution before and after template removal

$MITiO_2$ sensors

Figure 4 shows that $MITiO_2$ sensor with TiO_2/PTM ratio of 10/1 after template removal had an Δf value of 11.0 Hz responding to 9.88 μM of PTM solution, which was higher than the 4.0 Hz of TiO_2 NIP. This demonstrated that PTM molecular cavities were likely imprinted in the $MITiO_2$ sensor. Figure 5 shows the changes of resonance frequency (Δf) of $MITiO_2$ sensors with different ratios of TiO_2/PTM responding to 9.88 μM of PTM solution before and after template removal. After template removal, $MiTiO_2$ sensors had higher response to PTM than those before template removal. When ratio of TiO_2/PTM was 5/1, the $MITiO_2$ sensor reached the highest response to PTM. When the percentage of template molecules in the preparation ad-mixture was too high, the formed TiO_2 film after template removal could easily collapse due to insufficient TiO_2 quantity in the film.

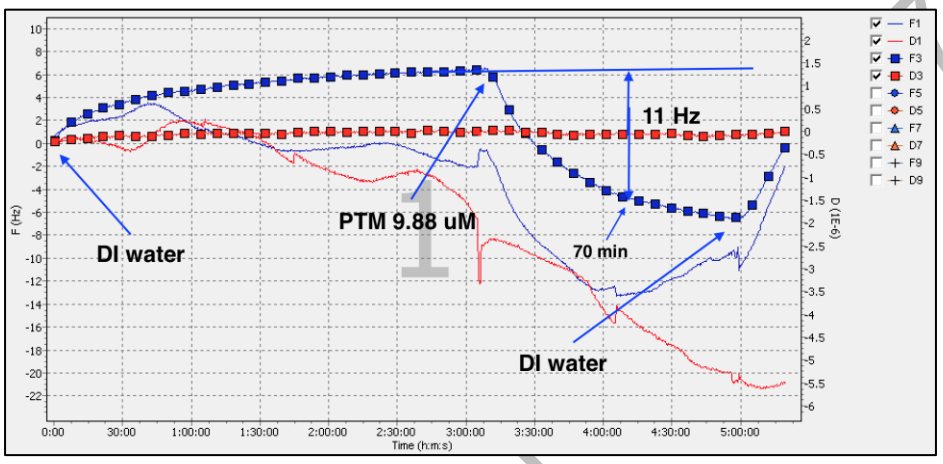

Figure 4. Change of resonance frequency (3rd overtone, i.e. the blue line with squares) of a $MITiO_2$ sensor after template removal; TiO_2: PTM = 10:1. The 1st fundamental frequency (the blue line without squares) was not stable and so could be ignored. Red lines were changes of resonance dissipation that were not discussed here.

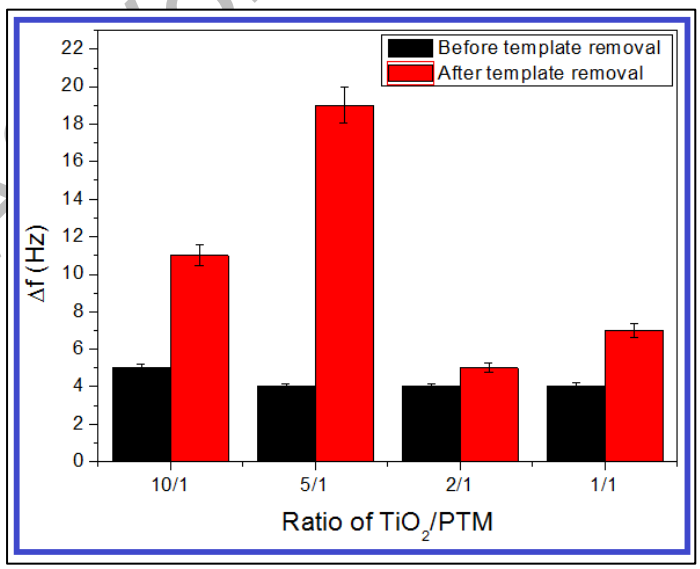

Figure 5. Changes of resonance frequency (Δf) of $MITiO_2$ sensors with different ratios of TiO_2/PTM responding to 9.88 μM of PTM solution before and after template removal by UV irradiation for 18 h

Figure 6 shows the changes of resonance frequency (Δf) of $MITiO_2$ sensor with 5/1 ratio of TiO_2/PTM with different UV irradiation time during template removal corresponding to 9.88 μM of PTM solution. With longer UV irradiation up to 36 hours, the sensor' response to PTM became weaker than that with only 18 hours of UV exposure. Superhydrophilicity of TiO_2 after UV exposure may explain this phenomenon. With 18 hours of UV irradiation, the superhydrophilicity of TiO_2 surface may reach a certain level but still could interact with hydrophobic PTM analyte molecules [19 – 21]. With further UV irradiation to 36 hours, the superhydrophilicity of TiO_2 surface continuously enhanced to a high level so that hydrophobic PTM analyte molecules had very weak interactions with TiO_2, resulting in poor response. Figure 7 further shows that $MITiO_2$ sensor had much higher response to PTM than non-imprinted TiO_2 (NIP).

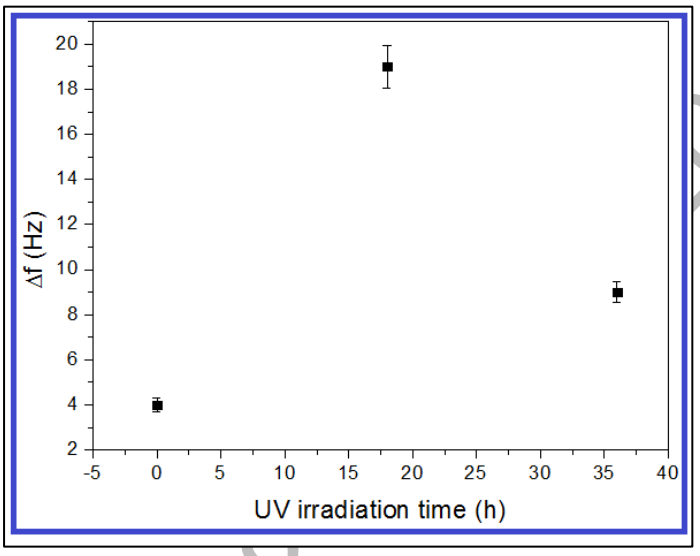

Figure 6. Changes of resonance frequency (Δf) of $MITiO_2$ sensor with 5/1 ratio of TiO_2/PTM with different UV irradiation time during template removal responding to 9.88 μM of PTM solution

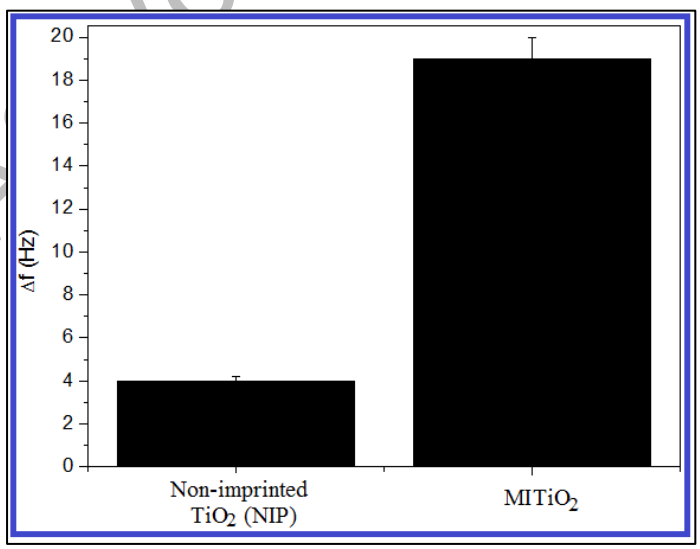

Figure 7. Changes of resonance frequency (Δf) of Non-imprinted TiO_2 (NIP) and $MITiO_2$ sensor with 5/1 ratio of TiO_2/PTM in the ad-mixture responding to 9.88 μM of PTM solution

Conclusion

Molecularly imprinted PVDF/TiO_2/PTM ($MIPTiO_2$) and TiO_2/PTM ($MITiO_2$) sensors were prepared and evaluated for the detection of parathion methyl, a simulant of chemical threat agents. Template PTM molecules were removed via photocatalytic degradation under UV irradiation with the existence of photocatalytically active TiO_2 nano crystals. Here we demonstrated that molecular cavities of PTM were formed inside the $MITiO_2$ sensor after PTM template molecules were removed. $MITiO_2$ with a 5/1 mass ratio of TiO_2/PTM in the ad-mixture showed promising sensing ability towards PTM analyte molecules after template removal. 18 h of UV irradiation time for template removal was sufficient while 36h was too long that superhydrophilicity of TiO_2 dominated and repelled the hydrophobic PTM analyte molecules resulting in lower response to PTM. Molecularly imprinted $MITiO_2$ sensors were suitable for the detection of CTAs and their simulants, such as PTM, with a good sensitivity. However, molecularly imprinted polymers $MIPTiO_2$ were not sensitive enough to be as sensors for CTAs and their simulants, possibly due to the incompatibility between hydrophobic PVDF and hydrophilic TiO_2.

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