Hybrid Nanocomposite-Based QCM Sensor for Detecting DMMP

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ABSTRACT

Taking a hybrid nanocomposite of nitrogen doped multi-walled carbon nanotube/cobalt oxide nanoparticle/gold nanoparticle as a sensing material, we developed a quartz crystal microbalance-based nerve simulant sensor. The sensor was simply fabricated by a drop casting of a mixture of the nanocomposite and ethanol on the top of gold electrode in a quartz crystal microbalance (QCM). Dimethyl methylphosphonate (DMMP) vapor as a targeted nerve simulant was generated by a bubbler system and modulated by two mass flow controllers. The frequency shifts taken from QCM was linearly responded to DMMP concentrations, ranging from 20 to 120 ppm. The adsorption rate of DMMP molecules was relatively high, while the desorption rate was low. It reveals a high sensitivity to DMMP vapor. To investigate the selectivity various VOCs including ethanol, water, toluene, methanol, and n-hexane were tested at 120 ppm of targeted VOCs concentration. Interestingly, the targeted VOCs other than DMMP were relatively low detected by the QCM sensor, implying remarkable selectivity. In this regards, the developed hybrid nanocomposite is a potential material to be used for sensing nerve simulants.

1. INTRODUCTION

Enabling sensitive and selective detection of various chemical species such as chemical warfare agents (CWAs) is highly desirable for the efficient use of both military and civilian defense resources.

Nerve agents, a part of CWAs are highly toxic and caused to death by inhibiting rapidly and irreversibly the activity of the enzyme acetyl cholinesterase due to the toxic accumulation of the neurotransmitter acetylcholine. Furthermore, nerve agents are quite stable and easily dispersed. In this regards, sensitive and selective detection of nerve agents are urgently demanded. To date the available nerve agent detectors utilize technologies that are adapted from classical analytical chemistry techniques. These technologies include ion mobility spectroscopy, flame photometry, infra-red spectroscopy, Raman spectroscopy, surface acoustic wave, colorimetric, photo ionization and flame ionization.

DMMP is commonly used as a nerve simulant because of its nontoxicity and organophosphorus compound with elemental composition that mimics nerve agents such as soman and sarin.

The carbon nanotubes have been used as attractive materials for sensing various chemical vapors due to their high aspect ratio in nanoscale, large surface area, good chemical stability, and excellent mechanical and electronic properties. In general, the developed CNT-based gas sensors reveals rapid response time, high sensitivity, low operating temperature and miniaturization.

In this study, we used a hybrid nanocomposite as a sensing material which is nitrogen doped MWCNT/cobalt oxide/gold (N-MWCNT/Co_3O_4/Au) for detecting DMMP by a QCM sensor.

2. EXPERIMENT DETAILS

To functionalize MWCNTs (0.5 mg) were dispersed in a mixture of H_2SO_4/HNO_3 (80 ml) with a volume ratio of 3:1, and then sonicated for 1h. The dispersed MWCNTs was heated at 80 ℃ for 6 h and neutralized with water. The resultant products of MWCNTs were filtrated through a PTFE membrane filter (pore size 0.2μm) and dried in a vacuum oven at 80℃ for 24 h. Finally, the carboxylic functionalized MWCNTs were collected in air tight bottle to avoid exposing to moisture.

To synthesize the nanocomposite the functionalized MWCNTs (0.25g) were dispersed in a mixture of water (50 ml) and urea/ammonia base (0.9 g, pH=9), and stirred for 4h. Then, cobalt cholride (2.9 g) was added and stirred at 90 ℃ for 12 h. Gold cholride (0.02 g) was further added, followed by reduction using a formic acid. The resultant product (N-MWCNT/Co_3O_4/Au) was collected and repeatedly purified by ethanol, followed by calcination at 180 ℃ for 12 h.

Finally, the nanocomposite dispersed in ethanol was coated on the quartz crystal by a drop casting and sonicated for 2 h.

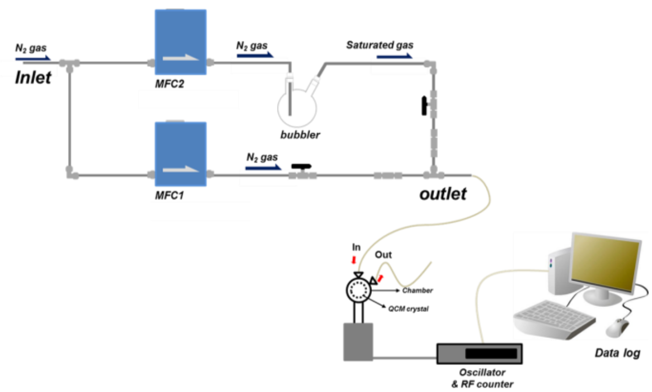

Figure 1. Schematic of QCM sensing system

A gas controller system for delivering DMMP vapor is shown in Figure 1. DMMP vapor was generated by a bubbler. The concentration of DMMP vapor was modulated by regulating flow rate of carrier gases using two mass flow controllers (MFCs, KOFLOC). Pure N_2 was used for both carrier and dilute gas.

Frequency shifts generated from the nanocomposite coated on QCM sensor were measured at room temperature by QCM 200 digital controller (Stanford Research System, SRS). The excitation of the QCM quartz (AT-cut 5 MHz quartz crystal with Cr/Ag electrode on both sides) was done by QCM 25 Crystal Oscillator (Stanford Research System, SRS).

3. RESULTS AND DISCUSSION

The real-time measurements of DMMP detection were performed in a range of DMMP concentration from 20 to 120 ppm. After each exposure to DMMP, the QCM chamber was purged with pure N_2 to allow the sensor to reset.

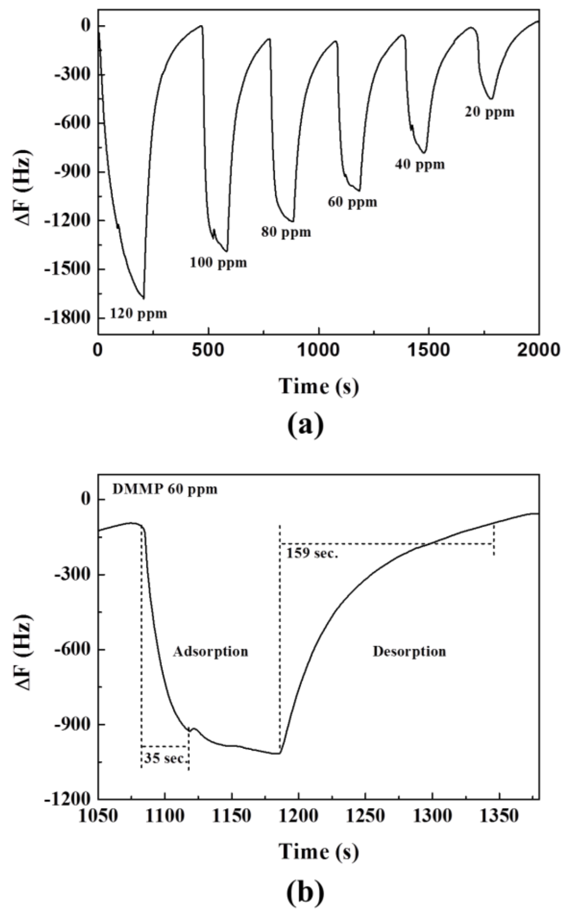

Figure 2. Frequency shift of N-MWCNT/Co_3O_4/Au-based QCM sensor as a function of DMMP concentration (a) and adsorption and desorption rate at 60 ppm of DMMP concentration.

Figure 2 shows frequency shift of the N-MWCNT/Co_3O_4/Au-based QCM sensor as a function of DMMP concentration. It indicates that the maximum frequency shift under 120 ppm of DMMP concentration occurs at 1682 Hz. The frequency shifts is linearly responded to DMMP concentrations, ranging 20 to 120 ppm. It reveals a high sensitivity to DMMP vapor. To compare the adsorption and desorption time at 60 ppm of DMMP concentration, a point of the saturated frequency shift (90% of maximum frequency shift) was taken, resulting in 35 s and 159 s, respectively. Compared to the desorption rate, the adsorption rate is quite high. The origin of the lower desorption rate is not clear and further investigation should be clarified.

To investigate the selectivity various VOCs including ethanol, water, toluene, methanol, and n-hexane were tested at 120 ppm of targeted VOCs concentration. Interestingly, as shown in Figure 3, the targeted VOCs other than DMMP were relatively low detected by the QCM sensor, implying remarkable selectivity.

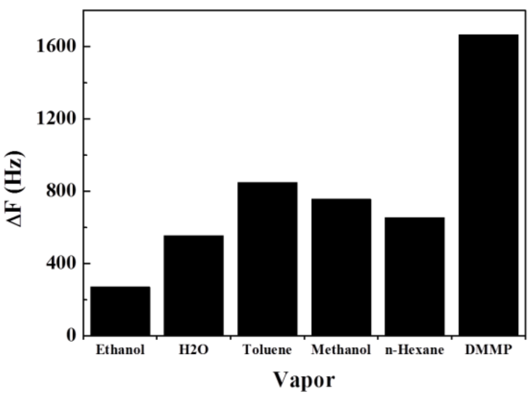

Figure 3. Comparison of the responses of the N-MWCNT/Co_3O_4/Au-based QCM sensor to ethanol, H_2O, toluene, methanol, n-hexane, DMMP.

4. CONCLUSION

A quartz crystal microbalance-based nerve simulant sensor was developed using a hybrid nanocomposite (N-MWCNT/Co_3O_4/Au) as a nerve agent simulant (DMMP) sensing material. The frequency shifts is linearly responded to DMMP concentrations, ranging 20 to 120 ppm. The adsorption rate of DMMP is high at a higher level of concentration, while the desorption rate is relatively low. However, the selectivity of VOCs is remarkable. It indicates that the developed nanocomposite will be a potential material for detecting various CWAs including nerve agents.

Further investigations will be needed towards the capability of CWAs detection at a low level of VOCs concentration.

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BIOGRAPHIES

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