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CONTENTS

- Evaluation of the Suitability of Fly Ash Powder for Atmospheric Plasma Spray 1 - 8
Mohd Moesli Muhammad, Azman Jalar, Roslinda Shamsudin & Mahdi Che Isa
- Electrochemical Imprinted Sol-Gel Films for Detection of Organophosphate Chemical Warfare Agent 9 - 16
Wan Norfazilah Wan Ismail & Atsunori Matsuda
- A Review of Techniques for the Detection of Biological Warfare Agents 17 - 26
Gian Marco Ludovici, Valentina Gabbarini, Orlando Cenciarelli, Andrea Malizia, Annalaura Tamburrini, Stefano Pietropaoli, Mariachiara Carestia, Michela Gelfusa, Alessandro Sassolini, Daniele Di Giovanni, Leonardo Palombi, Carlo Bellecci & Pasquale Gaudio
- Performance Analysis of a Minimum Configuration Multilateration System for Airborne Emitter Position Estimation 27 - 41
Ahmad Zuri Sha'ameri, Yaro Abdulmalik Shehu & Winda Asuti
- Development of a Pulse Repetition Interval (PRI) Modulation Template Using Walsh-Hadamard Transform (WHT) 43 - 50
Kamaruddin Abdul Ghani, Kaharudin Dimiyati & Ahmad Zuri Sha'ameri
- Evaluation of the Effect of Global Positioning System (GPS) Satellite Clock Error via GPS Simulation 51 - 62
Dinesh Sathyamoorthy, Shalini Shafii, Zainal Fitry M Amin, Asmariah Jusoh & Siti Zainun Ali
- Network Probe Patterns Against a Honeynet in Malaysia 63 - 75
Nogol Memari, Shaiful Jahari Hashim & Khairulmizam Samsudin
- EncryptDecrypt v1.0: A Cryptographic Application for Sending Messages via Commercial Email Providers 76 - 89
Nur Izyan Nabila Komori & Mohamad Ismail Ali
- Multi-Criteria Decision Making (MCDM) for Technical Evaluation of Tenderers: A Review of Methods Employed 90 - 102
Nor Hafizah Mohamed, Hendrik Lamsali & Dinesh Sathyamoorthy



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ELECTROCHEMICAL IMPRINTED SOL-GEL FILMS FOR DETECTION OF ORGANOPHOSPHATE CHEMICAL WARFARE AGENT

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ABSTRACT

The present study was undertaken to detect organophosphate chemical warfare agents via electrochemistry by utilising a molecular imprinted (MIP) sol-gel hybrid 3-cyanopropyltriethoxysilane (CNPrTEOS) film on indium tin oxide (ITO) glass substrate. The MIP film was formed by dip-coating on the ITO glass substrate through strong Si-O-Si bonds for selective, rapid and ultra-trace detection of organophosphate chemical warfare agent in a cyclic voltammetry (CV) device. The surface morphology and coating thickness of the MIP sol-gel hybrid CNPrTEOS film was characterised by using field emission scanning electron microscope. The blocking/insulating property of the MIP sol-gel hybrid film was studied using ferricyanide ions redox couple measurement. The CV peak current in the presence of different concentrations of the selected analyte showed a good linear correlation ($R^2 = 0.9977$) in the range 0.5 to 10 pg mL⁻¹ with a limit of detection (signal to noise ratio = 3) of 0.2446 pg mL⁻¹.

Keywords: *Sol-gel hybrid; molecular imprinted (MIP) film; electrochemical sensor; cyclic voltammetry (CV); organophosphate chemical warfare agent.*

1. Introduction

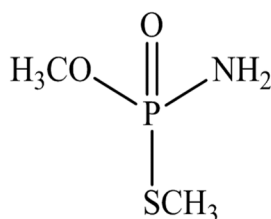
A number of organophosphate insecticides such as methamidophos, malathion and parathion are nerve agents acting on the enzyme acetylcholinesterase (AChE). Irreversible inhibition of AChE can result in possible death of humans (Newmark, 2004). Organophosphate insecticides are considered to be chemical warfare agents or chemical weapons if they are produced and stockpiled in amounts that exceed the requirements for purposes that are not prohibited under the Chemical Weapons Convention (CWC). There is an incidence of nerve agents being used as chemical weapons in human history and many countries. They were used against the Kurds in Iraq (Black *et al.*, 1994) and also in the terrorist attack on the Tokyo subway in 1995 (Nozaki & Aikawa, 1995). Research into new chemical weapons, their production and use still continue in different areas around the world (Bismuth *et al.*, 2004).

The determination and quantification of chemical warfare agent in a precise, convenient and economical fashion is an important goal that has been achieved only partially as these chemicals can be difficult to detect by conventional means (Noort *et al.*, 2002; Sadik *et al.*, 2003; Fitch *et al.*, 2003; Stewart & Sullivan Jr., 1992). In many cases, when chemical warfare agents or chemical weapons are present as contaminants, the first handling step is extraction followed by separation of the matrices before attempting to identify the types of chemicals present in the sample via a detector. Separation techniques such as liquid chromatography (LC), (Wada *et al.*, 2006) gas chromatography (GC) (Haas, 1998) and capillary electrophoresis (Nassar *et al.*, 1999) have proven successful methods for chemical warfare agent sample separation. These separation techniques are usually coupled to mass spectroscopy (MS) as a detection method (Kimm *et al.*, 2002; Wada *et al.*, 2006). Due to their physical properties, the method of choice for chemical warfare agents' analytical handling is GC-MS (Diaz *et al.*, 2004), where it is the only approved technology for nerve agent identification by the Organization for the Prohibition of Chemical Weapons (OPCW). Although GC-MS has some

advantages over LC-MS, such as its simple mobile phase which avoids issues such as reagent incompatibility, pH and solvent mix (Guodong & Lin, 2006), LC-MS is a good alternative for analysis of chemical weapon aqueous samples. Unfortunately, these laboratory techniques require large pieces of equipment, controlled conditions and highly trained personnel to conduct such experiments.

Electrochemical detectors have the potential to overcome the shortcomings associated with the present detection technologies. In electrochemical sensors, a working electrode is used to measure the electrochemical response of the system in the form of either potential or current signal. Measurements are often carried out in solution in the presence of an analyte by using the electrochemical properties of the nerve agent or of a chemical reaction that can be detected electrochemically (Wang *et al.*, 2008). Electrochemical detectors are potentially sensitive and selective and can be used for continuous monitoring. They also exhibit a wide linear response, minimal space and power requirements and are cost efficient.

In the present study, a cyano-based sol-gel hybrid film was constructed and molecularly imprinted (MIP) with selected organophosphate chemical warfare agent namely, methamidophos, for sensing applications. The novel cyano-based MIP sol-gel hybrid film was coated on indium tin oxide (ITO) glass substrate as a working electrode in cyclic voltammetry (CV) test for the detection of polar methamidophos with $\log K_{o/w} = -1.74$. The MIP and reference non-imprinted polymer (NIP) sol-gel hybrid film-coated ITO glass were used as the working electrodes to record the oxidation peak currents by CV in the phosphate buffer solutions (PBS) containing methamidophos (Scheme 1). The detector has been tested with respect to sensitivity, linearity and detection limit.



Scheme 1: Chemical structure of methamidophos.

2. MATERIALS AND METHODS

2.1 Reagents

3-cyanopropyltriethoxysilane (98%, CNPrTEOS) was purchased from Sigma Aldrich (St. Louis, MO, USA) and tetraethoxysilane (95%, TEOS) from Wako Pure Chemical Ind., Ltd. (Osaka, Japan). Hydrochloric acid (HCl) and deionised water were used for hydrolysis of functional monomers in polymerization process. The deionised water was obtained from a Millipore 106 Simplicity 185 (UV) water system from Thermo Scientific (Barnstead, MA, USA). Potassium ferricyanide (K₃Fe(CN)₆) was purchased from Wako Pure Chemical Ind., Ltd. (Osaka, Japan). Methamidophos (98.5%) was purchased from Sigma Aldrich (St. Louis, MO, USA). The standard stock solution was prepared by dissolving the standard pesticides in ethanol and kept at 4°C until used. They were diluted to required concentration using 0.05 M phosphate buffer solution (PBS). 0.1M potassium chloride (KCl) was used as a supporting electrolyte. All analyte solutions were prepared daily in 0.05M PBS (pH 7.0) and purged with nitrogen for 10 min prior to use. Other reagents were commercially available as analytical grade reagents and used without further purification.

2.2 Equipment

Cyclic voltammetry measurements were performed using an electrochemical analyser model HSV-100 (Hokuto Denko Co. Ltd., Tokyo, Japan) connected to a personal computer. A homemade electrochemical cell (5 mL), fitted with a gas bubbler and a three-electrode configuration consisting of indium tin oxide (ITO)-coated glass substrates (20 mm × 5 mm × 1.1 mm, 10 Ω/sq, Avan Strate Inc.) as working electrodes, a platinum wire, 2 cm long with a diameter of 0.3 mm as counter electrode and Ag/AgCl (saturated KCl) as a reference electrode. A field emission scanning electron microscope (FE SEM, Hitachi S-4800, Hitachi High-Tech., Tokyo, Japan) was used to characterize the surface morphology and thickness of the film.

2.3 Electrode Preparation and Procedures

2.3.1 Imprinted Sol-Gel Film Preparation

The sol-gel hybrid CNPrTEOS film was synthesised by drop wise addition of 0.67 mL of tetraethoxysilane (TEOS, 30% v/v) into 5 mL sample bottle containing 1 mL 0.10 M hydrochloric acid (HCl) as catalyst in 2.16 mL water. 2.4 mL cyanopropyltriethoxysilane (CNPrTEOS) was added dropwise into the same volume of HCl and water. Each solution was stirred for 45 min, and then the TEOS solution was poured into the CNPrTEOS solution. The mixture was further stirred at 450 rpm for 30 min. The homogenous CNPrTEOS sol was aged at room temperature before used in molecularly imprinting process. All procedures were conducted at room temperature. The MIP was prepared by thoroughly mixing a 4.5 mL of sol-gel hybrid CNPrTEOS sol obtained with 0.5 mL of 10 pg mL⁻¹ ethanolic methamidophos for 15 min. The remaining sol-gel hybrid CNPrTEOS sol was used for the reference non-imprinted film (NIP), with the same procedure was applied.

2.3.2 Pretreatment and Modification of ITO-Coated Glass Substrate

Before coating with the MIP and NIP sol-gel hybrid film, the ITO glass substrate was cleaned with RCA solution (Kern & Puotinen, 1970), rinsed with deionized water and dried using nitrogen gas blowing. The ITO glass substrate was covered with a strip of clear tape to achieve an uncovered electrode surface area of 50 mm² before dip-coating with the MIP or NIP sol-gel hybrid CNPrTEOS sol. The dip coating process was performed using a dip coater (DC4200, Aiden Co. Ltd., Shinshiro, Japan) at a constant rate of 0.1 mm s⁻¹. After the dip-coating process, the clear tape was removed. The MIP sol-gel hybrid CNPrTEOS-coated ITO glass was air-dried for 30 min before rinsed with the PBS to remove any physically adsorbed materials.

Methamidophos was removed from the imprinted film using ultrasonic desorption in ethanol for 2 min. Then the electrode was rinsed with deionized water and dried under nitrogen flow before use. Reference NIP film was rinsed with ethanol to remove any unreacted materials.

2.3.3 Electrochemical Measurements

The sol-gel film-coated ITO glass was dipped in 3 mL of appropriate concentrations of methamidophos in PBS (pH 7.0) for 7 min with stirring (150 rpm) at room temperature for pre-concentration effect. Then, the sol-gel hybrid film-coated ITO glass was washed with distilled water to remove any physically absorbed compounds on the electrode surface, before transferred into the electrochemical cell. The electrolyte solution was purged with nitrogen for 10 min before electrochemical measurements. CV measurements of methamidophos were recorded in 0.05 M PBS (pH 7.0) and 0.1 M KCl in the potential range of -1.0 to +1.2 V vs. Ag/AgCl at a scan rate of 100 mV s⁻¹. The blocking/insulating properties of the MIP sol-gel hybrid film was studied in the presence of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ redox couple measurements in the potential range of -0.2 V to +0.6 V at a scan rate of 100 mV s⁻¹. All measurements were performed at room temperature in triplicates.

3. RESULTS AND DISCUSSION

3.1 Preparation of the Modified Electrode

Glass substrate coated with ITO film is able to conduct electricity, thus it is very useful in CV measurement. In addition, pretreatment of ITO-coated glass substrate by Radio Corporation of America (RCA) method (Kern & Puotinen, 1970) has activated the ITO surface and allowed the MIP sol-gel hybrid film to covalently bind to the ITO film on the glass substrate (Gao *et al.*, 2007). Such bonding will enhance the lifetime of the modified working electrode as compared to physically coated film onto commonly used electrode such as glassy carbon electrode (Xie *et al.*, 2010; Li *et al.*, 2005).

The use of MIP technique in electrochemical sensing field has become a very important tool to develop suitable recognition elements with specific recognition sites (Atta & Abdel-Mageed, 2009; Yang *et al.*, 2009; Li *et al.*, 2012). Some of them are cavities with sizes matching the template molecule. These are template recognition sites, constructed with regular and perfect shape in the polymerization period and thus have good affinity for the template molecule (Li *et al.*, 2012). The other reason for the observed high selectivity of the template molecules is the presence of functional monomers in the polymer matrix which form specific binding cavities by leaving the template molecule from the polymers. The specific binding cavities matched with the template molecules, similar to the active sites in an enzyme (Hu *et al.*, 2012).

The use of hybrid film is a very significant factor in material design. CNPrTEOS possesses hydroxyl and cyano-group that can form hydrogen bond with amino-group in methamidophos and also allow polar interaction with polar methoxy and methylthio group in methamidophos. The propyl group in CNPrTEOS introduces additional hydrophobicity to the resultant materials. It is known that the hybrid film is able to promote the rebinding ability of template molecules to the imprinted film (Shustak *et al.*, 2003; Marx *et al.*, 2004; Pater *et al.*, 2009). On the contrary, there are no imprinted cavities in the reference NIP sol-gel hybrid film that could be opened, thus it shows poor current responses. TEOS used in this study provided strong Si-O-Si bonds with the treated ITO glass, which effectively prevents the sensor film from flake off.

The use of the dip coater in this study, at a constant rate is to form a thin uniform film. Thickness of film is one of the most effective factors that affect the sensitivity of the MIP sol-gel hybrid film (Firenman-Shoresh *et al.*, 2005). Although thicker film would increase the amount of methamidophos imprinted onto the sol-gel hybrid film, however it will slow the penetration of methamidophos towards the electrode and delay the detection time. Therefore, in this study, the dip coating process was performed only once. The thickness of the film obtained was ~149 nm.

3.2 Characterisation and Evaluation of Molecularly Imprinted Sensor

The blocking/insulating properties of the MIP sol-gel hybrid film (methamidophos template removed and unremoved) was studied in the presence of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple measurement in the potential range from -0.2 V to +0.6 V to ensure that the sol-gel hybrid film has successfully be imprinted with the methamidophos template when there are cavities produced and allowed the penetration of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ ions from the electrolyte towards the working electrode (Hu *et al.*, 2012; Sharma *et al.*, 2012). Bare gold (Au), glassy carbon electrode (GCE) and ITO glass were used as reference working electrode in the blocking/insulating properties study. The $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox peaks observed using reference electrodes were compared with the new developed working electrode. Cyclic voltammogram at the Au, GCE and ITO glass showed a relatively well defined redox peaks with peak potential difference (ΔE_p) of 221, 361 and 171 mV, respectively. The peak potential of GCE is highest among the three electrodes (Figure 1a), which may be contributed to the slow kinetics of the electron transfer on carbon (Liu *et al.*, 2005). In Figure 1b, redox peaks were recorded using a reference NIP and the MIP sol-gel hybrid CNPrTEOS film (methamidophos template removed and unremoved). A couple of similar redox peaks of $[\text{Fe}(\text{CN})_6]^{3-}/\text{Fe}(\text{CN})_6]^{4-}$ as when using reference electrodes were observed using the MIP sol-gel hybrid CNPrTEOS film after

removal of methamidophos template. This suggested that MIP sol-gel hybrid CNPrTEOS film had successfully been synthesized on the ITO glass surface and cavities were produced in the MIP sol-gel hybrid CNPrTEOS film as a result of the template methamidophos removal (Fang *et al.*, 2009; Huang *et al.*, 2011). No response could be observed with both the NIP ITO glass and MIP sol-gel hybrid CNPrTEOS-coated ITO glass (before methamidophos template removal). The result shows that the NIP film and methamidophos template on MIP film have retarded the electron transfer between the electrolyte and the electrode. There is no difference in the cyclic voltammograms obtained in the presence or absence of methamidophos template, indicating that methamidophos does not exhibit any electroactivity in the potential range chosen (-0.2V to +0.6V).

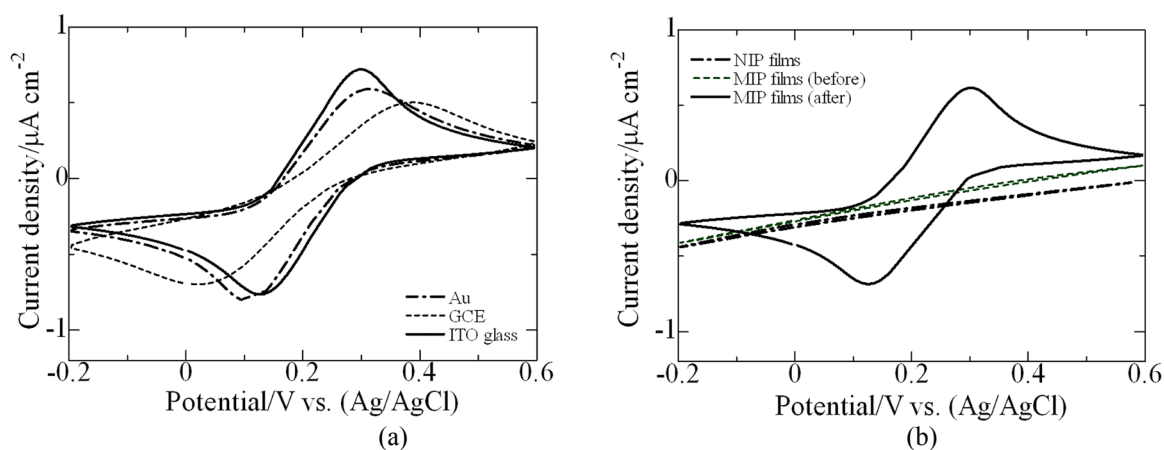


Figure 1: Cyclic voltammogram of 0.01M $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.10 M KCl using (a) reference bare gold, glassy carbon electrodes and ITO glass and (b) reference NIP sol-gel hybrid CNPrTEOS-coated ITO glass substrate, MIP sol-gel hybrid CNPrTEOS-ITO glass electrodes before and after removal of methamidophos template.

FE SEM was applied to characterise the surface morphology of the sol-gel hybrid film-coated ITO glass. From Figure 2, both films shows smooth surface when characterized at low magnification ($\times 50\text{K}$). Higher magnification at $\times 100\text{K}$ shows that the surface of MIP sol-gel hybrid film, before undergo the desorption process in ethanol under ultrasonic irradiation, are uniformly and homogeneously disperse MIP sol-gel hybrid particles (Figure 2a) while Figure 2b shows cavities caused by the removal of methamidophos template. These cavities can selectively bind with the target molecules (methamidophos) and allow them to penetrate freely.

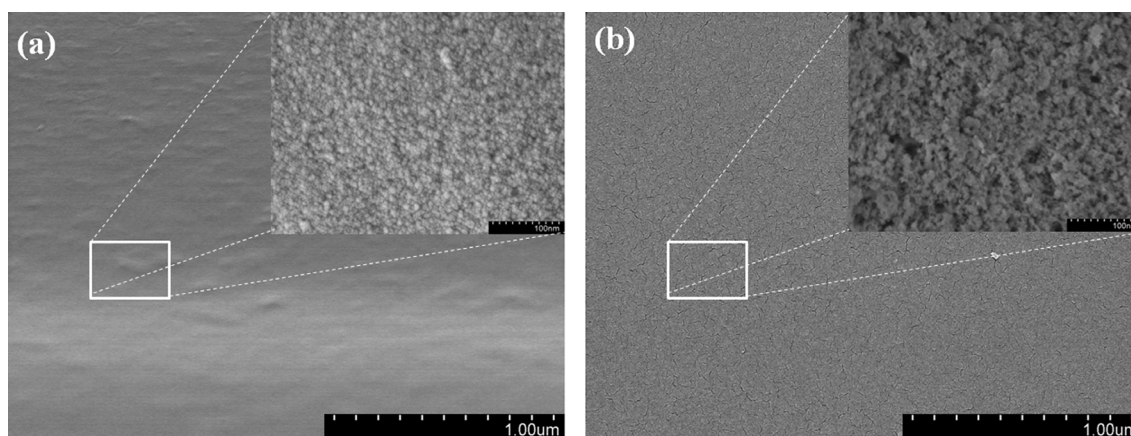


Figure 2: FE SEM micrographs of MIP sol-gel hybrid CNPrTEOS surfaces for (a) before (magnification: $\times 50\text{K}$ and $\times 100\text{K}$) and (b) after template removal (magnification: $\times 50\text{K}$ and $\times 100\text{K}$).

3.3 Electrochemical Detection of Methamidophos

Figure 3 illustrates the CV responses for increasing methamidophos concentration in 0.05 M PBS (pH 7.0) containing 0.1 M KCl. The linear range, limit of detection (LOD) (S/N=3) and standard deviation for methamidophos using MIP sol-gel hybrid CNPrTEOS were 0.5 to 10 pg mL^{-1} , 0.25 pg mL^{-1} (part-per-trillion) and 4.04% (n = 7), respectively. The detection limit achieved is very important to detect ultra trace level of pesticides in samples with complex matrix.

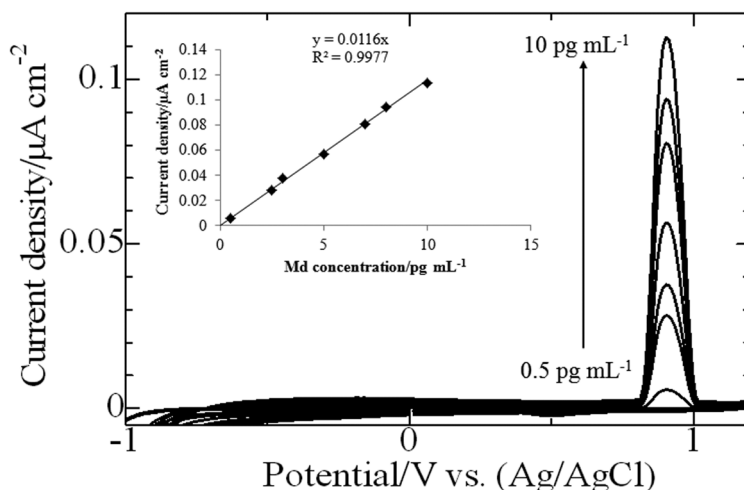


Figure 3: Cyclic voltammograms of increasing methamidophos concentration in 0.05 M PBS (pH = 7) containing 0.1 M KCl. The inset shows the calibration curve of methamidophos. Methamidophos concentration was 0.5, 2.5, 3.0, 5.0, 7.0, 8.0, 10.0 pg mL^{-1} , respectively. Scan rate: 100 mV s^{-1} .

4. CONCLUSION

This work demonstrated a sensitive, rapid and simple electrochemical sensor for detection of polar organophosphate chemical warfare agent which was successfully developed by using sol-gel hybrid molecular imprinted technology. Analysis of polar analyte is challenging as they are soluble in water and polar solvent. The ability of the synthesized sol-gel hybrid CNPrTEOS Md MIP film as an electrochemical sensor for the detection of methamidophos was successfully demonstrated. Sol-gel hybrid CNPrTEOS as functional monomer for methamidophos recognition was coated onto the ITO glass substrates and significantly exhibited excellent sensitivity and selectivity for the template molecule rebinding. Under selected analytical conditions, the electrochemical sensor shows very low detection limit down to part per trillion level (pg mL^{-1}) which seems to be a promising tool for trace-level detection of organophosphate chemical warfare agent. Alternatively, the preparation of MIP sol-gel hybrid CNPrTEOS-coated ITO glass for other template molecules could be also easy with the procedure described in this study.

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