Landmine detection: Improved binding of 2,4-dinitrotoluene in a γ-CD/metal oxide matrix and its sensitive detection *via* a cyclic surface polarization impedance (cSPI) method†

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Received (in Cambridge, UK) 1st March 2007, Accepted 20th March 2007
First published as an Advance Article on the web 5th April 2007
DOI: 10.1039/b703132g

Highly sensitive and selective detection of 2,4-DNT, a representative explosive, was achieved by the synergic effect of molecular imprinting and host (cyclodextrin)–guest interaction in ultrathin layers of TiO_2 and SiO_2 gel; the detection limit using cSPI measurements reached nM concentration.

Methods currently used to detect buried landmines mostly depend on metal detectors and well-trained dogs. However, the metal detector is less effective for finding landmines when they are made from plastics and alternative materials. In addition, they are apt to be disturbed by other metal fragments in the soil. On the other hand, well-trained dogs (canines) are extremely effective for finding buried landmines, but this requires much time and cost for training, and dogs get tired rather readily. Therefore, more efficient techniques are desired for sensing buried landmines.[1]

Most landmines contain nitro-aromatic explosives such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT). Therefore, buried landmines can be detected by taking advantage of such structural features. A variety of chemical approaches based on fluorescent, electrochemical, piezoelectric and absorption-spectral properties have been investigated in recent years.[2] Among them, the use of fluorescent polymers has enabled the low concentration detection of explosives in air and soil samples.[3]

Recently, a Kyushu University group has developed a novel electrochemical analytical method based on impedance measurements *via* cyclic surface polarization.[4] This cyclic surface polarization impedance (cSPI) method can detect the adsorption and desorption of chemical substances onto the electrode by measuring electrochemical impedance with stepwise changes of electrode potential.[4] In their previous attempt, the electrode surface was modified with anthracene, which could form charge transfer (CT) complexes with nitro-aromatic compounds.[5] The cSPI measurement with this electrode was useful for detecting nitro-aromatic compounds selectively, but its detection limit still remained at a sub-μM level.

It occurred to us that higher sensitivity and selectivity could be attained by combining molecular imprinting and receptor effects. Receptor molecules such as cyclodextrins (CDs), calixarenes and other recognition modules have been employed to enhance the sensing ability of polymer-based sensing interfaces.[6] CD hosts are effective for the incorporation of nitro-aromatic compounds.[7] Very recently we have introduced CD hosts into TiO_2 ultrathin layers for the better detection of nitro-aromatic compounds.[8]

Surface modification of the Pt electrode was confirmed by quartz crystal microbalance (QCM) (9 MHz) experiments. Fig. 1 shows QCM frequency shifts during the imprinting procedure of 2,4-DNT. The frequency shift was 16 ± 3 Hz for $Ti(O–^nBu)_4$, 28 ± 2 Hz for a γ-CD/2,4-DNT mixture and 48 ± 1 Hz for $Si(OMe)_4$. The adsorption density of the γ-CD/2,4-DNT mixture could be calculated from the QCM frequency shift of the adsorbed mass, and corrected for the molecular weight (MW: 1479.25) of a 1 : 1 γ-CD/2,4-DNT complex and the surface area of the electrode (0.159 cm^2). The complex occupies an adsorption density of 0.32 molecules nm^{-2}. This value corresponds to 71% of the theoretical adsorption density of γ-CD, 0.45 molecules nm^{-2}, which can be calculated by assuming a close packed monolayer of the cylindrical receptor with an outer diameter of 16.9 Å. The incorporated 2,4-DNT in the complex was removed by treatment with methanol for about 30 min at 25 °C ($-\Delta F = 5 \pm 1$ Hz, where ΔF is the frequency shift). Additionally, each step of the film

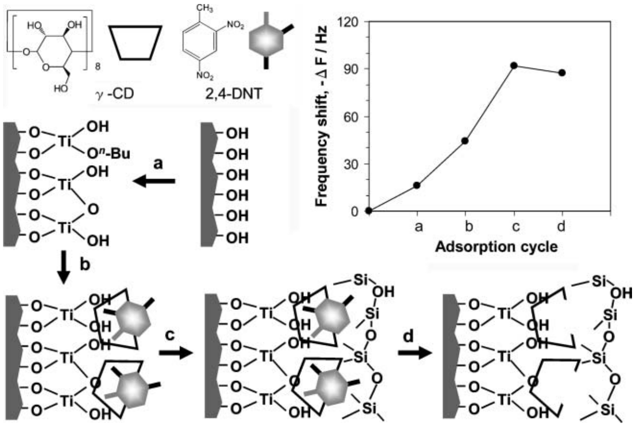

Fig. 1 Reaction scheme and QCM frequency shifts during the surface modification procedure of 2,4-DNT. (a) $Ti(O^nBu)_4$ adsorption and hydrolysis, (b) adsorption of a γ-CD/2,4-DNT mixture, (c) $Si(OMe)_4$ adsorption and (d) template removal.

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† Electronic supplementary information (ESI) available: Detailed experimental conditions and FT-IR spectral data. See DOI: 10.1039/b703132g

assembly process and the adsorption of 2,4-DNT were analyzed by FT-IR measurements by the spectral change of the nitro stretch (N=O) peak at around 1348 cm^{-1} (see Figs. S1–S5†). The intensity changes of the IR peak at 1348 cm^{-1} were consistent with the change in impedance responses observed by a cSPI system (see Fig. S6†).

Electrochemical impedance (R_P) was measured by scanning of both the frequency (260 to 35 Hz) and the electrode potential, where the impedance change (ΔR_P) due to the electrode potential change represents a chemical sensor output. Details of the measurement and data analysis are described in our previous studies.[4,5] Fig. 2 shows response profiles (ΔR_P) to 2,4-DNT and the concentration dependence of $|\Delta R_p|$ (−0.15 V) on the TiO_2/γ-CD/SiO_2 (2,4-DNT removed) Pt electrode. It was found that benzene and other aromatic compounds without specific functional groups were strongly adsorbed onto the Pt, irrespective of the electrode potential, and the impedance change symmetrically increased, except for around −0.1 V at the pzc (potential of zero charge) of Pt.[5] This is attributed to the interaction between the aromatic ring and the Pt surface by π-orbital overlap.[9] In contrast, the response profile of the TiO_2/γ-CD/SiO_2 (2,4-DNT removed) Pt-electrode gave a characteristic peak at around −0.15 V, and the peak height increased in proportion to the concentration of 2,4-DNT. It is possible to detect 2,4-DNT molecules at 2×10^{-9} to 2×10^{-7} M. The detection limit appears to be lower than 1×10^{-9} M. Interestingly, the magnitude of this impedance change is about two times larger than that of the TiO_2/γ-CD film over the given concentration range (see the inset of Fig. 2). This fact suggests that γ-CD molecules on the surface offer stronger binding sites for 2,4-DNT by the aid of a SiO_2 coating layer. It is clear that the templated film provides a useful transducer surface for the detection of 2,4-DNT in cSPI measurements.

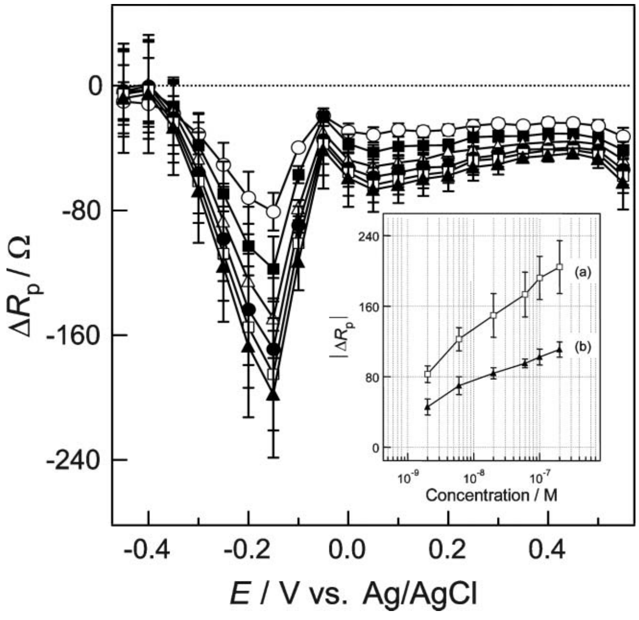

Fig. 2 Response profiles to 2,4-DNT on a TiO_2/γ-CD/SiO_2 (2,4-DNT removed) Pt electrode: (○) 2×10^{-9} M, (■) 6×10^{-9} M, (△) 2×10^{-8} M, (●) 6×10^{-8} M, (□) 2×10^{-7} M and (▲) 6×10^{-7} M. The inset shows the concentration dependence of $|\Delta R_p|$ (−0.15 V) on (a) TiO_2/γ-CD/SiO_2 (2,4-DNT removed) and (b) TiO_2/γ-CD Pt-electrodes, respectively.

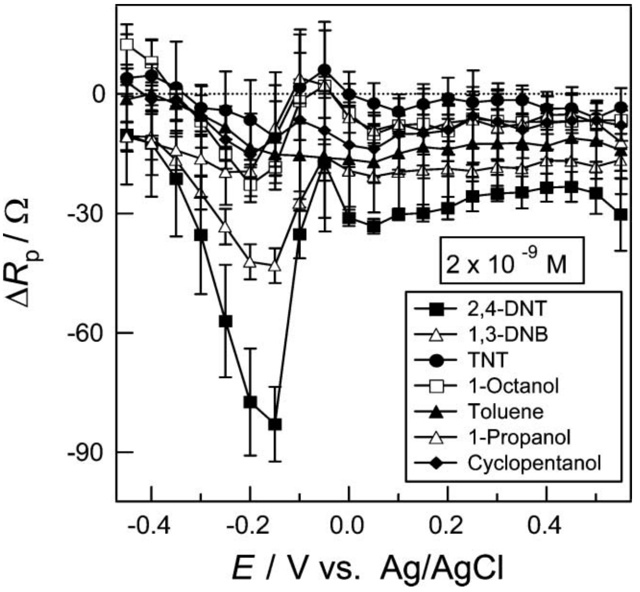

Fig. 3 Response profiles (2×10^{-9} M) of 2,4-DNT and related guest molecules on a TiO_2/γ-CD/SiO_2 (2,4-DNT removed) Pt-electrode.

Fig. 3 shows the electrochemical response of the TiO_2/γ-CD/SiO_2 (2,4-DNT removed) film with 2,4-DNT and related guest molecules at the very low concentration of 2×10^{-9} M. The templated film reveals higher selectivity towards 2,4-DNT and 1,3-dinitrobenzene (1,3-DNB) at −0.15 V, and lesser responses are observed with other structurally-related guest molecules. In particular, even if 2,4,6-trinitrotoluene (TNT) penetrates into the cavity of γ-CD, it is not bound efficiently. This indicates that the sensitivity and selectivity towards 2,4-DNT are created by a synergic effect of the host–guest interaction with the γ-CD molecule and the presence of the imprinted cavity.

In conclusion, a chemically modified cSPI sensor that combines a molecular imprinting effect and host–guest interaction in TiO_2 matrices can detect 2,4-DNT at nM (sub-ppb) concentrations in solution. Among the explosives used for landmines, 2,4-DNT shows a relatively high vapor concentration, close to or greater than 1 ppm in air.[10] This concentration is sufficiently high under laboratory conditions. However, we need to further examine the sensor response in the open air and in realistic environments. It may be necessary to improve the detection limit to the level of a few ppt for practical applications.

This work was supported by the 21st Century COE Program "Reconstruction of Social Infrastructure Related to Information Science and Electrical Engineering", CREST of the Japan Science and Technology Agency (JST), and the MEXT *via* the Kitakyushu Knowledge-Based Cluster Project.

Notes and references

1 J. Yinon, *Anal. Chem.*, 2003, **75**(5), 99A.
2 J. MacDonald, J. R. Lockwood, J. McFee, T. Altshuler, T. Broach, L. Carin, C. Rappaport, W. R. Scott and R. Weaver, *Alternatives for Landmine Detection*, RAND Corp., Santa Monica, CA, USA, 2003, pp. 15–47.
3 J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864; H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, *J. Am. Chem. Soc.*,

2003, **125**, 3821; A. Rose, Z. Zhu, C. Madigan, T. M. Swager and V. Bulovic, *Nature*, 2005, **434**, 876.

4 M.-J. Ju, K. Hayashi and K. Toko, *Sens. Mater.*, 2001, **13**, 169; K. Hayama, H. Tanaka, M.-J. Ju, K. Hayashi and K. Toko, *Sens. Mater.*, 2002, **14**, 443; M.-J. Ju, K. Hayama, K. Hayashi and K. Toko, *Sens. Actuators, B*, 2003, **89**, 150.

5 K. Masunaga, K. Hayama, T. Onodera, K. Hayashi, N. Miura, K. Matusumoto and K. Toko, *Sens. Actuators, B*, 2005, **108**, 427.

6 K. D. Schierbaum, T. Weiss, E. U. Thoden, T. Velzen, J. F. J. Engbersen, D. N. Reinhoudt and W. Göpel, *Science*, 1994, **265**, 1413; F. L. Dicker and R. Sikorski, *Mater. Sci. Eng., C*, 1999, **10**, 39.

7 X. Yang, J. Shi, S. Johnson and B. Swanson, *Langmuir*, 1998, **14**, 1505; X. Yang, X.-X. Du, J. Shi and B. Swanson, *Talanta*, 2001, **54**, 439.

8 M.-J. Ju, D.-H. Yang, S.-W. Lee, T. Kunitake, K. Hayashi and K. Toko, *Sens. Actuators, B*, 2007, **123**, 359.

9 F. Montilla, F. Huerta, E. Morallon and J. L. Vazquez, *Electrochim. Acta*, 2000, **45**, 4271; M. Saeys, M. F. Reyniers, G. Marin and M. Neurock, *J. Phys. Chem. B*, 2002, **106**, 7489.

10 C. L. Rhykerd, D. W. Hannum, D. W. Murray and J. E. Parmeter, *Guide for the Selection of Commercial Explosives Detection Systems for Law Enforcement Applications: NIJ Guide 100–99*, NIJ, USA, 1999, pp. 7–10, http://www.ncjrs.org/pdffiles1/nij/178913-1.pdf.