Anchoring of Cyclodextrin Units on TiO_2 Thin Layer for Effective Detection of Nitro-aromatics: A Novel Electrochemical Approach for Landmine Detection

Naoki Takahara,[1] Do-Hyeon Yang,[1] Myung-Jong Ju,[2] Kenshi Hayashi,[2] Kiyoshi Toko,[2]
Seung-Woo Lee,*[1] and Toyoki Kunitake[1,3]
[1]*Graduate School of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Kitakyushu 808-0135*
[2]*Graduate School of Information Science and Electrical Engineering, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581*
[3]*Frontier Research System (FRS), The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako 351-0198*

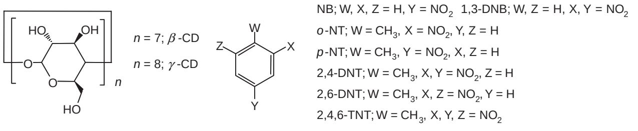
(Received August 11, 2006; CL-060925; E-mail: leesw@env.kitakyu-u.ac.jp)

Nitro-aromatic compounds could be sensitively detected by employing cyclic voltammetric experiments in ultrathin TiO_2 gel/cyclodextrin (CD) multilayered films that were prepared via the gas-phase surface sol–gel process. Among others, 2,4-DNT showed the highest voltammetric response for the γ-CD immobilized TiO_2 film and its detection limit was estimated to be less than nM levels.

More than 100 million landmines exist unexploded in 70 countries of the world and two million new landmines are additionally buried every year. Most of them are constructed without metallic parts and would therefore not be detected with metal detectors. There are urgent worldwide needs for the development of efficient and cost-effective landmine detectors with high sensitivity for actual explosive molecules. Various types of mobile devices such as mass spectrometer, gas chromatograph, and ion mobility spectrometer have been developed as handheld "sniffers" for landmine detection, and are called electronic "noses."[1]

Most landmines contain nitro-aromatic compounds such as 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (TNT) as explosives, so that buried landmines may be detected by taking advantage of such chemical structures. Chemical sensor approaches are advantageous in providing low-cost devices that have a wide spectrum of application by modifying mass-sensitive and optical transducers with a chemically sensitive layer. In particular, sensing devices based on host–guest interactions recently have attracted increasing attention because they are capable of sensitively detecting guest molecules by using the molecular recognition capability of host molecules.[2] Cyclodextrins (CDs) consist of six to eight D-glucopyranoside units, linked by a 1,4-glucosidic bond, and are known to form host–guest inclusion complexes with organic species in solution and in gas phase. On the other hand, the surface sol–gel process is capable of ready incorporation of effective receptors such as dendrimers, cyclodextrins, and polyrotaxanes.[3] Herein, we propose a novel approach for detecting nitro-aromatic explosives, which is based on the electrochemical assay of nitro-aromatic compounds (Scheme 1) captured in the cavities of alternately assembled cyclodextrins in TiO_2 ultrathin layers as a sensing interface.

In this study, deposition of TiO_2 ultrathin layers was conducted by the gas-phase surface sol–gel (GSSG) process that is valuable for the fabrication of ultrathin metal oxide films with controlled thickness from metal alkoxides in gas-phase.[4] First, titanium n-butoxide, $Ti(O\text{–}^nBu)_4$, was heated in a sealed bottle at 85 °C, and the vaporized $Ti(O\text{–}^nBu)_4$ was carried with nitrogen gas at a flow rate of 3 L/min. It was allowed to deposit on a mercaptoethanol-modified gold-coated QCM electrode (9 MHz, 0.159 cm^2 for one side) for 10 min, and the physisorbed alkoxide was removed by flushing nitrogen gas. Then the QCM electrode was immersed in deionized water for 1 min, dried with nitrogen gas, and the frequency was measured. Subsequently, the TiO_2 gel-deposited electrode was immersed in an aqueous solution (10 mM) of β-CD or γ-CD for 20 min at 30 °C and rinsed with deionized water, and the frequency was measured after drying with nitrogen gas. This alternate deposition of TiO_2 gel and β-CD or γ-CD layers was repeated 10 times.



Scheme 1.

Figure 1 shows QCM frequency changes due to the alternate adsorption. The QCM frequency linearly decreases with adsorption cycles, indicating regular growth of the TiO_2/CD multilayer film. Average frequency changes were 8 ± 3 Hz for the adsorption of $Ti(O\text{–}^nBu)_4$ and 15 ± 5 Hz for that of both β-CD and γ-CD. From the QCM data, the adsorption density of β-CD and γ-CD molecules was calculated as 0.2_2 and 0.2_0 molecules/nm^2, respectively, corresponding to 41–44% of their theoretical adsorption densities of 0.5_4 and 0.4_5 molecules/nm^2. The latter values can be calculated by assuming close-packed monolayers of cylindrical receptors with diameters of 15.3 Å (for β-CD) and 16.9 Å (for γ-CD). Therefore, β-CD and γ-CD molecules are assembled with a similar coverage of ca. 40% on the TiO_2 gel layer. The remaining 60% will be covered with a TiO_2 gel layer. The ΔF value of 8 Hz for the adsorption of $Ti(O\text{–}^nBu)_4$ corresponds to a thickness increase of ca. 0.13 nm for the whole TiO_2 gel layer, using the density of bulk TiO_2 gel (1.7 g/cm^3).[3] In the case of 60% coverage, the maximal layer thickness is estimated to be 0.22 nm on the open (not covered by CD molecules) surface.

Figure 2A shows cyclic voltammograms (CVs) of ferricya-

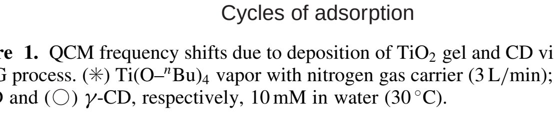


Figure 1. QCM frequency shifts due to deposition of TiO_2 gel and CD via the GSSG process. (✳) $Ti(O\text{–}^nBu)_4$ vapor with nitrogen gas carrier (3 L/min); (●) β-CD and (○) γ-CD, respectively, 10 mM in water (30 °C).

nide, $Fe(CN)_6{}^{3-}$, on a bare QCM electrode and on the $(TiO_2/\beta\text{-CD})_{10}$ and $(TiO_2/\gamma\text{-CD})_{10}$ modified QCM electrodes.[5] Both of the TiO_2/CD films gave reversible redox peaks similar to that of the bare electrode in the potential range from −0.3 to 0.6 V, although the separation of peak potential, ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$), is larger than that of the bare electrode. These peaks are attributed to the electrochemical process of the ferricyanide/ferrocyanide redox system. Lower currents are observed for both of the TiO_2/CD films than for the bare electrode. This suggests that the immobilized CD molecules and/or the TiO_2 gel matrix act as barrier against transport of ferricyanide as electroactive probe. Ferricyanide ion would not be included in the cavity of β-CD or γ-CD because of its larger size, and the TiO_2 gel surface that is effective for the electroactive probing will be lessened. Interestingly, the current decrease is larger for γ-CD than for β-CD, even though the surface coverage by CD molecules was almost the same. This indicates that the resistance of the films is closely related to the cavity size: 8.5 and 9.5 Å for β-CD and γ-CD, respectively.

It has been reported that immobilized CD molecules are capable of selective transport of various organic species via host–guest interaction.[6] In many cases, ferrocenes and quinines are used as electroactive guest molecules. In this work, we intended to use ferricyanide as an indirect probe to evaluate the access of guest molecules to the cavity of CD molecules. Differential pulse voltammetry (DPV) was adopted to record the reduction current at different concentrations of 2,4-DNT guest in the potential range from 0.1 to 0.5 V (Figure 2B). Before the potential was applied, 2,4-DNT was allowed to form complexes inside the CD cavity. For both of the β-CD and γ-CD modified electrodes, the DPV current was enhanced with the increase in the concentration of 2,4-DNT in the range of 2.0×10^{-9} to 1.0×10^{-6} M. The current increase showed a better linearity and was much larger for γ-CD than for β-CD (data not shown). The current observed here results from the reduction of ferricyanide molecules that could be activated by the access of 2,4-DNT to the CD cavity.

In order to make a quantitative comparison with other guest molecules, the same DPV experiment was carried out at the guest concentration of 1.0×10^{-7} M. The results are shown in Figure 3 in which the graphical presentation shows the current difference ($\Delta I\text{p}/\mu\text{A}$) before and after addition of guest molecules. Very interestingly, similar effects are found for both the β-CD and γ-CD films. The electrochemical activity of ferricyanide is enhanced with aromatic and nitro-aromatic compounds, whereas it is suppressed slightly by aliphatic compounds (1-propanol, cyclopentanol, and adamantanol). It appears that aromatic and nitro-aromatic compounds, especially 2,4-DNT and 2,6-DNT, captured in the CD cavity promote electron transport from the electrode.

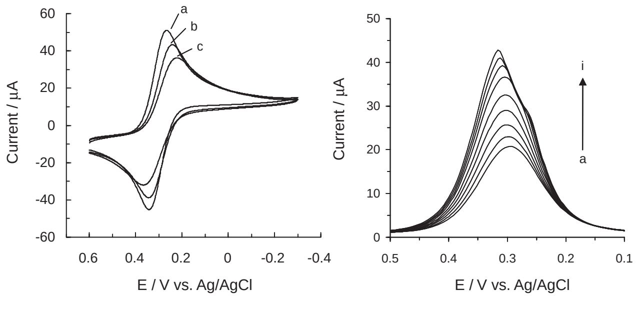


Figure 2. (A) Cyclic voltammograms of ferricyanide on a bare QCM electrode (a) and on $(TiO_2/\beta\text{-CD})_{10}$ and $(TiO_2/\gamma\text{-CD})_{10}$ modified QCM electrodes (b and c, repectively). (B) Differential pulse voltammograms of ferricyanide on the $(TiO_2/\gamma\text{-CD})_{10}$ modified QCM electrode at different concentrations of 2,4-DNT. (a) 0 M, (b) 2.0×10^{-9} M, (c) 1.0×10^{-8} M, (d) 2.0×10^{-8} M, (e) 5.0×10^{-8} M, (f) 1.0×10^{-7} M, (g) 2.0×10^{-7} M, (h) 5.0×10^{-7} M, and (i) 1.0×10^{-6} M. Scan rate was $0.05\ \text{V s}^{-1}$.

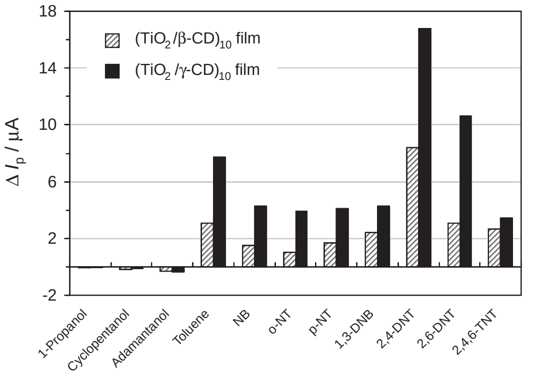


Figure 3. DPV current changes before and after addition of guest molecules (1.0×10^{-7} M).

In conclusion, nitro-aromatic compounds could be detected sensitively by the enhancement of the reduction current of ferricyanide in ultrathin TiO_2 gel/CD multilayered films, whereas aliphatic compounds increased the resistance of the films. Among others, 2,4-DNT showed the highest voltammetric response for the γ-CD immobilized TiO_2 film and its detection limit was estimated to be less than nM levels. This demonstrates that a sensitive sensor for nitro-aromatic compounds can be constructed based on the alternate assembly of CD molecules in TiO_2 gel layers. Recently, Yang et al. reported the detection of nitro-aromatic explosives using cyclodextrin polymer films on surface acoustic wave (SAW) devices and found that the sensitivity and selectivity can be greatly enhanced by introducing electron-rich aromatic moieties to CD molecules.[7] Since DNT and TNT contain electron-withdrawing nitro groups on the aromatic benzene ring, they are apt to show strong interaction towards the synthetic CD receptors. This effect would induce a higher sensitivity of nitro-aromatic compounds in the current sensor system. Although we still need to examine the role of selective guest inclusion in the ultrathin TiO_2 gel matrix, this new approach should be applied to the detection of a variety of organic molecules.

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