Electronic Supplementary Information (ESI):

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 (*c*SPI) method

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Experimental Conditions

Modification of Pt electrodes. Pt electrodes were polished with alumina slurry (Buehler number 3, 0.05 μm particle size), subjected to sonication for 10 min in deionized water, and then exposed to the flame of a Bunsen burner. After this cleaning treatment, the Pt electrodes were modified with a self-assembled monolayer of 6-mercaptohexanol (10 mM in ethanol, 6 h). The hydroxyl-terminated Pt electrode was then immersed in 100 mM $Ti(O–{}^{n}Bu)_4$ in toluene/ethanol (1:1) for 10 min at 25°C, rinsed thoroughly with ethanol, and then subjected to hydrolysis in deionized water and drying with N_2 gas flushing. The working electrode (Pt) was then immersed in a solution of γ-CD (1 mM) or γ-CD/2,4-DNT complex (1 mM each) in water for 3 h at 40°C and rinsed with deionized water. Subsequently, the γ-CD/2,4-DNT complex on the TiO_2 ultrathin layer was covered with a SiO_2 layer by immersing the electrode in 100 mM $Si(OMe)_4$ in water for 1 h at 25 °C. Finally, the incorporated 2,4-DNT in the complex was removed by treatment with methanol for about 30 min at 25°C, followed by rinsing with deionized water and drying with N_2 gas.

QCM measurements. A quartz crystal microbalance (QCM, 9 MHz) device manufactured by USI System, Fukuoka, Japan, was used for monitoring film assembly and template removal. A gold-coated QCM resonator was treated with piranha solution (96.0% sulfuric acid/30.0–35.5% hydrogen peroxide, 3/1, v/v), rinsed with deionized water, and dried with N_2 gas. The film assembly was also carried out onto such QCM electrodes by a procedure essentially identical with that used in the case of Pt-electrodes. QCM frequency was measured with a Hewlett-Packard 53131 A counter (255 MHz), where a frequency decrease of 1 Hz corresponds to a mass increase of ca. 0.9 ng, according to the Sauerbrey equation.[1]

cSPI measurements. The cSPI sensor system consists of a handmade potentiostat and a frequency response analyzer (FRA, NF Electronic Instruments 5020).[2–4] A three-electrode cell was used in the cSPI method. Three electrodes; working electrode (WE), reference electrode (RE) and counter electrode (CE), are connected to a potentiostat and dipped in a test solution. The alternating input voltage was generated by the FRA and was superimposed to the electrode potential that is controlled by the potentiostat. The amplitude and phase difference between input and output signals were measured with the FRA. The electrochemical impedance was then calculated by the ratio of amplitude and the difference of phase between the input voltage and the output current. The measurement process was controlled by a computer through GPIB.

The measurement set-up was made up according to the previously reported method.[3] The WE was fixed on the acrylic board through a 0.2 mm thick silicone rubber with a 2 mm diameter hole. The WE and the CE were a polycrystalline Pt plate (10 mm × 20 mm and 0.5 mm in thickness) and Pt wire, respectively. The RE was an Ag/AgCl electrode with saturated KCl solution. While the electrode potential was swept from 0.45 to – 0.55 V in 0.05 V steps, electrochemical impedance was measured at f_L = 45Hz and f_H = 260 Hz to evaluate the real part (R_p) and the imaginary part (X_p) of the CPE impedance as described previously.[3] The supporting electrolyte solution was 10 mM KCl. All cSPI measurements were carried out at room temperature.

Assessment of film assembly. FT-IR was used to assess each step of the film assembly process. TiO_2 gel was prepared by the hydrolysis of $Ti(O–{}^{n}Bu)_4$ in ethanol. The prepared TiO_2 gel powder was thoroughly ground using an agate mortar and pestle and then allowed to react with CD molecules (1 mM each for α, β and γ) and a CD/2,4-DNT mixture (1:1, 1 mM each for α, β and γ), respectively. Subsequently, the CD/2,4-DNT-modified TiO_2 gels were modified with $Si(OMe)_4$ (100 mM in water). The samples that were dried under vacuum overnight were mixed with potassium bromide (KBr) at 1 wt%. The KBr mixtures were homogenized and then pressed into a transparent KBr pellet using a press. Infrared spectra were obtained for bare TiO_2 gel, CD-modified TiO_2 gel, CD/2,4-DNT-modified TiO_2 gel, and SiO_2-coated CD/2,4-DNT-modified TiO_2 gel using an FT-IR spectrometer FTIR 8400S (Shimadzu). All data were collected at a spectral resolution of 1 cm^{-1}.

Fig. S1 shows FT-IR spectra of 2,4-DNT and α-, β- and γ-CDs, respectively. In curve a of Fig. S1, two unique peaks at 1530 cm^{-1} and 1347 cm^{-1} correspond to the asymmetric and symmetric N=O stretches of the nitro group ($–NO_2$). On the other hand, the IR spectra of α-, β- and γ-CDs are almost the same in the whole range (curves b, c and d of Fig. S1). The peaks at around 3390 cm^{-1} and 2929 cm^{-1} are assigned to the O–H and $–CH_2–$ stretches of the CD molecules, respectively. In addition, the peaks in the range of 1456 cm^{-1} and 1399 cm^{-1}, corresponding to the in-plane $–CH_2–$ and O–H bending modes, further confirm the presence of the hydroxyl functional group. The peaks centered at 1158 and 1028 cm^{-1} are attributed to the C–O–C (ether) stretch of the glucose ring and

1,4-glycosidic unit of the CD molecules. The peak at around 1079 cm^{-1} may be assigned to the C–O stretch of the C–OH moiety.

FT-IR spectra of the bare TiO_2 gel and the CD-modified TiO_2 gel were shown in Fig. S2. In the FT-IR spectrum of TiO_2 gel (curve a of Fig. S2), a broad peak centered at 3231 cm^{-1} is assigned to be the stretching vibration of O–H at the surface of the TiO_2 gel. In the case of the CD-modified TiO_2 gels (curves b, c, and d of Fig. S2), the peak at 3367 cm^{-1} may be due to the vibration of the OH groups of the CD molecules. On the other hand, the peak intensity at 2929 cm^{-1} decreased because the stretching vibration of CH_2 for CDs adsorbed to TiO_2 surface is partially altered. In addition, the disappearance of the O–H stretching in the range of 1456 cm^{-1} and 1399 cm^{-1} can be strongly attributed the interaction with TiO_2 gel. Therefore, it can be expected that the CD molecules were chemically bound to the TiO_2 gel surface through the OH groups of CDs by chelating to the Ti (IV) at the surface of the TiO_2 particles.

Figs. S3 and S4 show FT-IR spectral changes due to the removal and rebinding of 2,4-DNT for γ-CD/2,4-DNT-modified and SiO_2-coated γ-CD/2,4-DNT-modified TiO_2 gels, respectively, in the frequency region of 2000–800 cm^{-1}. The key spectral change of the nitro stretching was confirmed at around 1533 (weak) and 1348 (strong) cm^{-1} (curve a in each case) and this will be of considerable use in the detection of buried landmines. On the other hand, these spectral features due to 2,4-DNT incorporation completely disappeared after the TiO_2 gels were rinsed with methanol (curve b in each case). No change was observed when the surface-modified TiO_2 gels were rinsed only with pure water. This indicates that the 2,4-DNT molecule could be efficiently removed by methanol rinsing. To confirm the binding of 2,4-DNT to γ-CD molecules, the γ-CD-modified TiO_2 gels after methanol treatment were immersed in a solution of 2,4-DNT (1 mM) in water for 30 min at room temperature and rinsed with deionized water. The incorporation of 2,4-DNT to the γ-CD cavity could be evident from the reproduction of the nitro stretching at 1348 cm^{-1} (curve c in each case). Interestingly, the adsorbed amount of 2,4-DNT, which is proportional to the intensity of the IR peak at 1348 cm^{-1}, increases by coating the surface of the γ-CD/2,4-DNT-modified TiO_2 gel with a SiO_2 layer. The γ-CD-anchored binding site shows an enhanced affinity for 2,4-DNT by the aid of a SiO_2-coating layer.

To clarify the adsorption mechanism of 2,4-DNT, we further examined IR spectral changes due to the adsorption of 2,4-DNT for different types of CD-modified TiO_2 gels. Fig. S5 shows FT-IR spectral changes due to adsorption of 2,4-DNT for (a) α-, (b) β-, and (c) γ-CD-modified TiO_2 gels, respectively, and (d) a SiO_2-coated γ-CD/2,4-DNT-modified (2,4-DNT removed) TiO_2 gel in the frequency region of 2000–800 cm^{-1}. There is no change at 1348 cm^{-1} for α-CD and the largest peak intensity was observed for the SiO_2-coated γ-CD/2,4-DNT-modified (2,4-DNT removed) TiO_2 gel. From the IR peak intensity at 1348 cm^{-1}, it is evident that the amount of 2,4-DNT adsorbed decreases in a sequence of γ-CD ≈ β-CD > α-CD. Especially, the immobilized γ-CD unit with

2,4-DNT can be covered and stabilized by an additional coating layer of SiO_2. Apparently, the templated site retains γ-CD units even when 2,4-DNT is removed by rinsing. The intensity changes of the IR peak at 1348 cm^{-1} for these modified TiO_2 gels are consistent with the change in impedance responses observed by a cSPI system (Fig. S6).

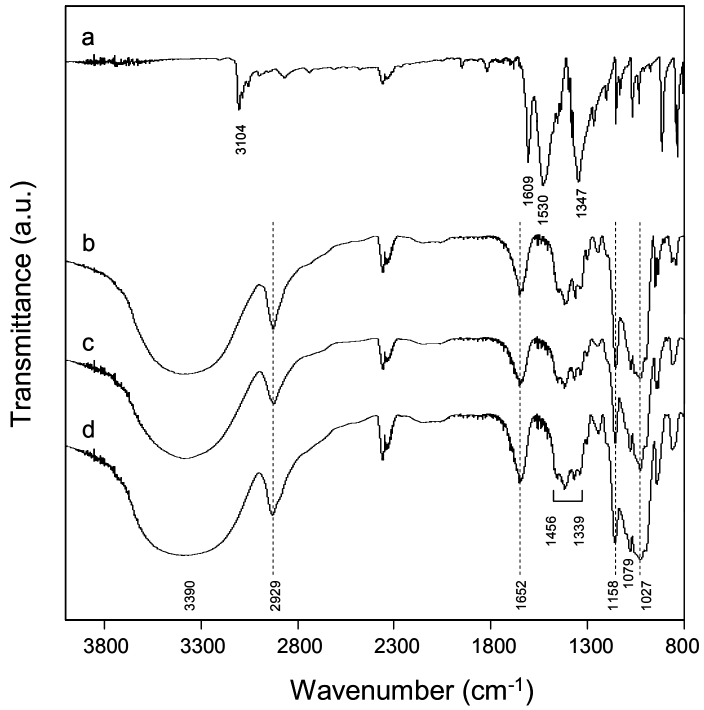

Fig. S1. FT-IR spectra of (a) 2,4-DNT and (b) α-, (c) β-, and (d) γ-CDs, respectively.

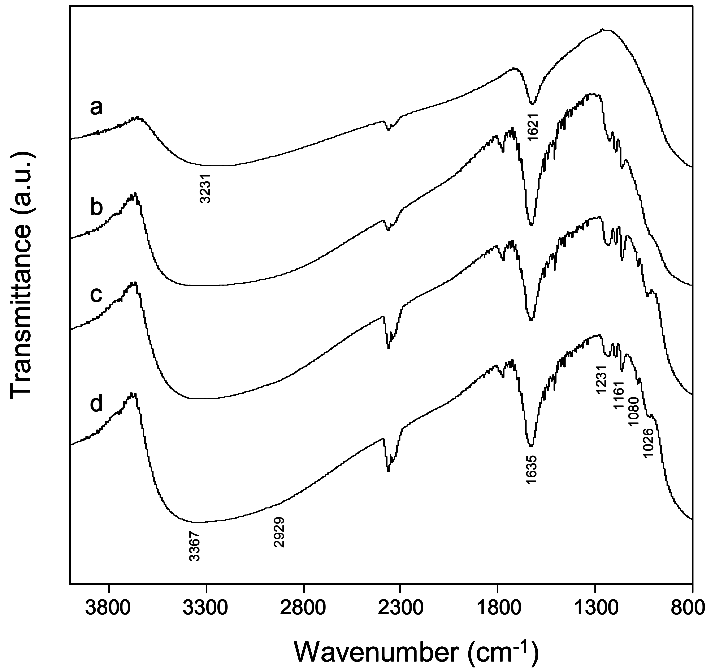

Fig. S2. FT-IR spectra of (a) bare TiO_2 gel and (b) α-, (c) β-, and (d) γ-CD-modified TiO_2 gels, respectively.

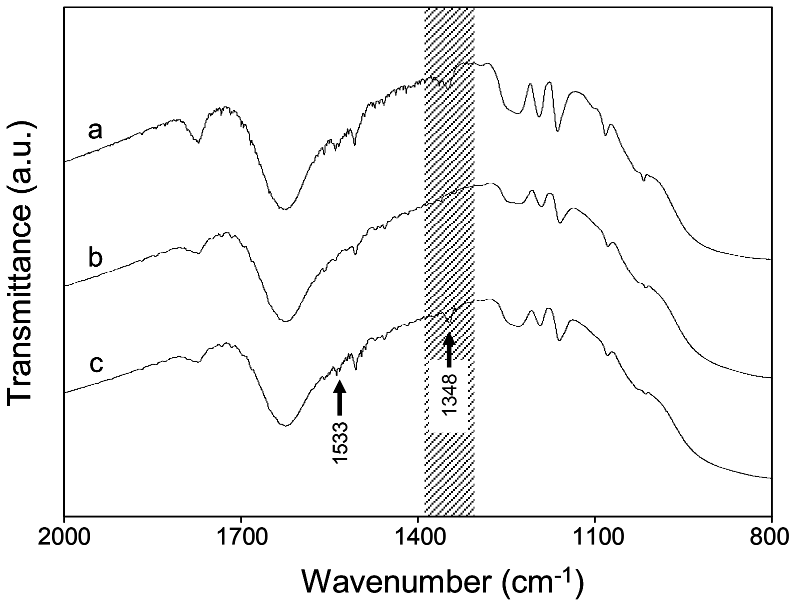

Fig. S3. FT-IR spectra changes due to removal and rebinding of 2,4-DNT for a γ-CD/2,4-DNT-modified TiO_2 gel: (a) before template removal, (b) after rinsing , and (c) after rebinding.

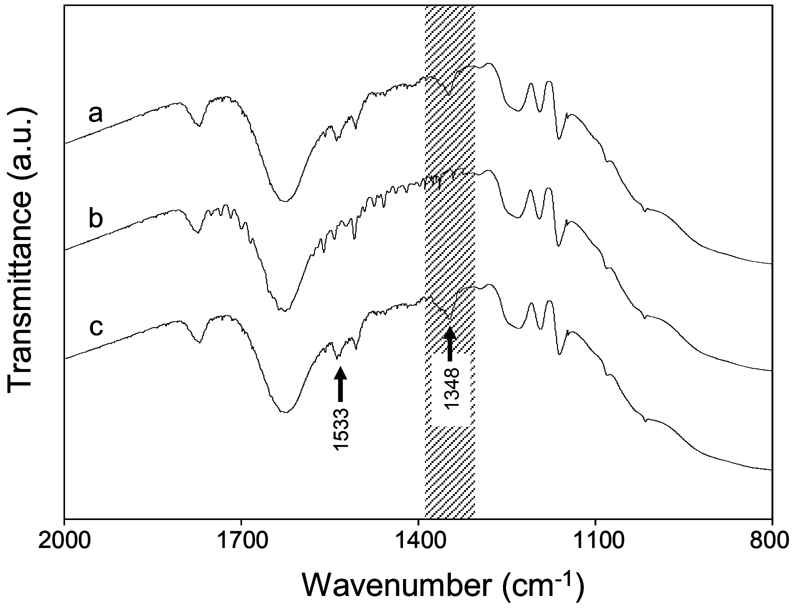

Fig. S4. FT-IR spectral changes due to removal and rebinding of 2,4-DNT for a SiO_2-coated γ-CD/2,4-DNT-modified TiO_2 gel: (a) before template removal, (b) after rinsing , and (c) after rebinding.

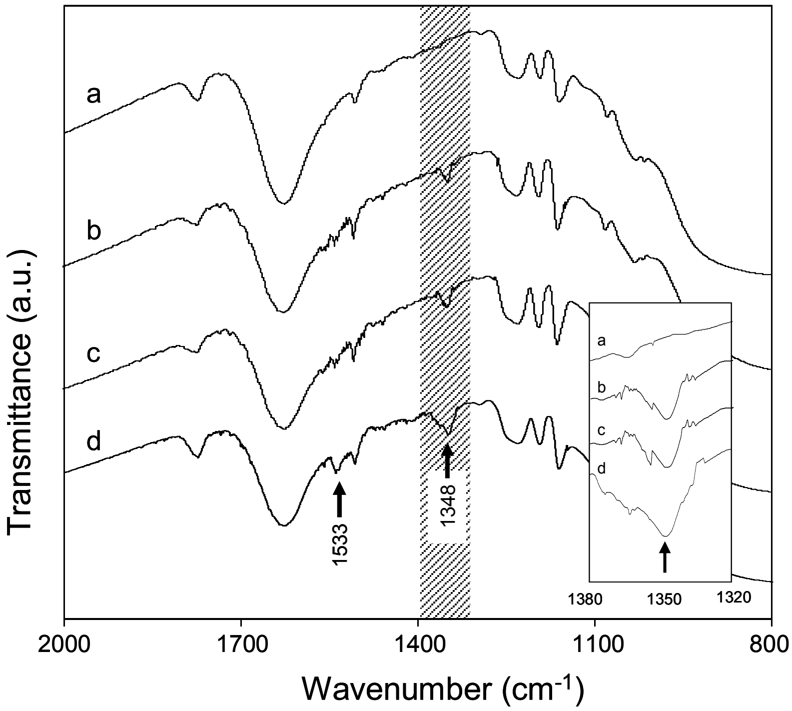

Fig. S5. FT-IR spectral changes due to adsorption of 2,4-DNT for (a) α-, (b) β-, and (c) γ-CD-modified TiO_2 gels, respectively, and (d) a SiO_2-coated γ-CD/2,4-DNT-modified (2,4-DNT removed) TiO_2 gel.

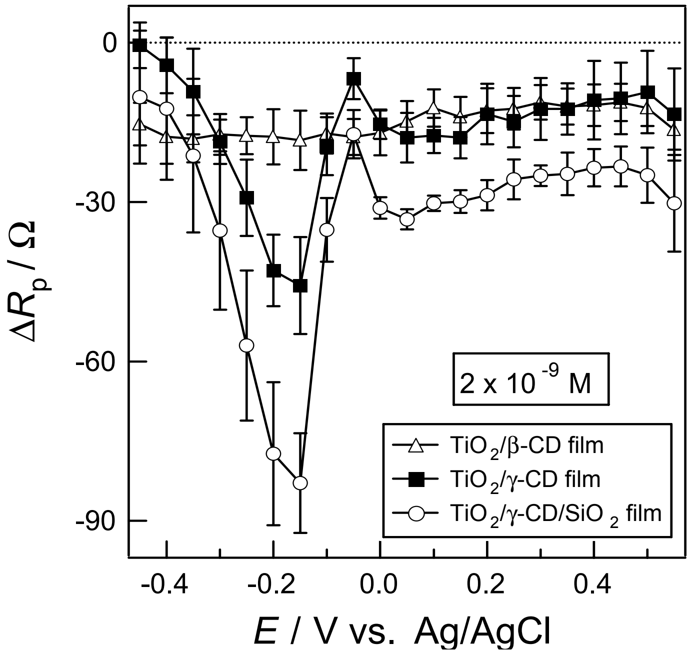

Fig. S6. Response profiles (2×10^{-9} M) of 2,4-DNT on (a) TiO_2/β-CD, (b) TiO_2/γ-CD, and (c) TiO_2/γ-CD/SiO_2 (2,4-DNT removed) Pt electrodes.

References

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