Electronic Supporting Information

for

Reduced graphene oxide film as matrix of MALDI-TOF-MS for detection of octachlorodibenzo-p-dioxin

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(1) Experimental

Chemicals and materials. The solution of octachlorodibenzo-p-dioxin (OCDD) (D-801S) in toluene ¹⁵ or n-hexane with a concentration of 50 μ g/ml (50 ppm) was purchased from AccuStandard (New Haven, Connecticut, USA). Graphite powder (SP-1) and carboxylated single-walled carbon nanotubes (SWCNTs) P3 were purchased from Bay Carbon (Bay City, Michigan, USA) and Carbon Solutions (Riverside, California, USA), respectively. Activated carbon powder, 2, 5-dihydroxybenzoic acid (DHB), α -cyano-4-hydroxycinnamic acid (CHCA) and sinapic acid (SA) were purchased from Sigma-²⁰ Aldrich (St. Louis, Missouri, USA).

Preparation of OCDD solution. The OCDD was dissolved in toluene or n-hexane at a concentration of 50 ppm, which was used to prepare other solutions with different concentrations (5 ppm, 500 ppb, and 50 ppb) after dilution. The volume of each diluted solution for MALDI analysis is 1 μ L. Therefore, the quantities of the analyte are 50 ng, 5 ng, 500 pg, and 50 pg, respectively.

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Preparation of rGO films. Graphene oxide (GO) was synthesized according to the modified Hummers method.^{1,2} Preparation of rGO film has been described in the previous report.³ In brief, GO dispersed in water was first centrifuged at 5000-6000 rpm for 30 min. By decanting the supernatant, the GO was redispersed in methanol with a concentration of ~1 mg/mL, which was spin-coated at 4000 s rpm onto a piranha-cleaned SiO₂ wafer. GO film in brown color was obtained, Figure S1a, which was then chemically reduced with a hydrazine vapor at 65 °C overnight to obtain rGO film with a thickness of ~ 20 nm, Figure S1b. Figure S2 shows the AFM image of the rGO thin film. XPS was used to measure reduction of GO film. Based on the XPS result, GO gives much oxygenated functional groups, while those functional groups were largely removed after GO was reduced to rGO. This result has been reported by us⁴ and others.



Figure S1. (a) GO film on SiO_2 obtained by spin-coating. (b) rGO film on SiO_2 after reduction of GO film with hydrazine vapor.



¹⁵ **Figure S2**. AFM image of rGO film used as matrix of MALDI-TOF-MS for detection of octachlorodibenzo-p-dioxin. Z scale: 80 nm.

Preparation of rGO powders. Based on the previously reported method,⁵ a suspension of GO in a mixed solvent of H₂O and DMF was obtained by sonicating GO in water (3 mg/mL, 2 mL) and then adding DMF (18 mL) to make GO concentration to be 0.3 mg/mL. The obtained brown GO suspension was reduced by addition of 100 μ L hydrazine and then heated at 80 °C for 10 h with stirring by using ⁵ the magnetic stir bar, to obtain the rGO suspension. Thus resulting black rGO suspension is stable and no precipitation was observed within days. In case the precipitation occurs, mild sonication of the suspension can exfoliate rGO. The suspended rGO powders are referred to as rGO powders. Figure S3 shows the SEM image of the rGO powders deposited on SiO₂ wafer.



Figure S3. SEM image of rGO powders.

Preparation of SWCNT film. The SWCNT film was prepared based on the previous reports.^{4,6} ¹⁵ Briefly, carboxylated-SWCNT was firstly well-dispersed in DI H₂O (0.2 mg/mL) with the assistance of probe sonication. The SWCNT film was obtained via phase-separation facilitated self-assembly of dispersed SWCNTs. The resulting film was then transferred to SiO₂ substrate used as matrix. Figure S4 shows the SEM image of the SWCNT film.



Figure S4. SEM image of the SWCNT film.

Preparation of samples for mass spectroscopy.

- s (i) The matrix, rGO film or SWCNT film on SiO₂, was adhered onto the ground-steel sample target plate by carbon tapes. Graphite or activated carbon powders were sonicated and dispersed in a saturated sucrose aqueous solution. The resulting mixture of sucrose and graphite (or activated carbon) was dropped onto the ground-steel sample target plate, used as matrix. Then the different quantities of OCDD were dropped on the matrix and dried. For example, if 500 ppg of OCDD was tested, 1 μL OCDD with a concentration of 500 ppb was deposited on the matrix. In our experiment, OCDD with different quantities of 50 ng, 5 ng, and 500 pg was tested.
- (ii) The rGO powders (0.3 mg/mL in DMF) were used as an adsorbent of solid-phase extraction and matrix. Four samples (**a-d**) were prepared. 100 μ L (**a**), 10 μ L (**b**), 5 μ L (**c**), and 1 μ L (**d**) of OCDD stock solution were firstly added to 40 μ L rGO suspension. After DMF was used to dilute the solution ¹⁵ to 500 μ L, the solution was mixed by vortexer (Bio Laboratories, Singapore) for 1 min. The OCDD was extracted from solution and adsorbed on the surface of rGO for 2 h. After the centrifugation of the above solution at 10,000 rpm and then removal of the supernatant, the rGO adsorbed with OCDD was precipitated at the bottom of centrifuge tube. Finally, DMF was added to the precipitate to get a 500 μ L solution.

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1 μ L from the 500 μ L final solution (**a-d**) was dropped on the steel plate, which was used for the mass analysis. The quantity of rGO used in samples **a-d** is 24 ng. The quantity of OCDD used in samples **ad** is 10 ng, 1 ng, 500 pg, and 100 pg, respectively.

⁵ **MALDI-TOF-MS instrument.** All the spectrometric measurements were performed on an Axima TOF^2 mass spectrometry (Shimazu/Kratos, Singapore). Each mass spectrometer uses a nitrogen laser at 337 nm (Pulse 10 ns, 10 Hz) for desorption of analytes. Each spectrum was recorded by adding 100 laser shots using a laser energy of 56.80 µJ. The accelerating voltage is 20 kV, and the operating pressure is 10^{-6} mbar. All the mass spectra shown here were obtained in a negative ion mode.

(2) Mass spectra of OCDD using other materials as matrix

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Figure S5 shows the mass spectra of OCDD by using graphite powders as matrix, indicating that 5 ng of OCDD could be detected. However, the peak intensity and signal-to-noise ratio are significantly lower than that obtained with rGO film as matrix (Figure 1a). The reason is, possibly similar to rGO ¹⁵ powders, that the graphite powders were not continuously connected when they were spread on the steel plate. Therefore, the energy does not well conduct through the powders and is not easily transferred to the analytes. Another possible reason for lower sensitivity is the lack of residual oxygen-containing functional groups, which are present on rGO to capture chloride radicals produced in the ionization process.



Figure S5. Mass spectrum of 5 ng OCDD on graphite powders.

Figure S6 shows the mass spectra of OCDD by using the activated carbon powders as matrix. 5 ng of $^{\circ}$ OCDD was tested. It is clearly seen that the peak intensity is very low, as compared to that in rGO film (Figure 1a). Therefore, the activated carbon is not a suitable matrix and cannot give higher efficiency of desorption/ionization for OCDD. Presumably, the activated carbon lacks the π -conjugated network, which absorbs energy and then transfers energy and electrons to analytes. Although the activated carbon powders have been successfully used as matrix for other molecules,⁷ they are not a suitable matrix for OCDD in our experiment.



Figure S6. Mass spectrum of 5 ng OCDD adsorbed on activated carbon powders. Inset: Amplified spectrum.

⁵ Recently, carbon nanotubes (CNTs) have been used as matrix for MALDI-TOF-MS.^{8,9} Figure S7 shows the results using SWCNT networks as the matrix to detect OCDD. Very weak signal is observed, which proves that the SWCNT film is not a suitable matrix for the OCDD detection.



Figure S7. Mass spectrum of 5 ng OCDD on SWCNT film.

Last but not least, in order to look for the suitable matrices for OCDD detection, other materials, other than carbon-based materials, have also been tried. For instance, silica particles, with size in hundreds of nm and surface functionalized with aminophenyl groups, were intensively studied in our group. Figure S8 shows the SEM image of the silica particle film.



¹⁰ Figure S8. SEM image of silica particle film.

Figure S9 shows the mass spectra of OCDD when silica particles, modified with and without carbon blacks, were used as matrices. The carbon black used here is CABOT 300, which is modified with 2-carboxyphenyl groups. The carbon black was used to improve the conductivity of silica particles to perform MLADI-TOF-MS for OCDD. Although the signals are observed, the detection limit of OCDD s is 1 ng, which is higher than that obtained in rGO film (500 pg). Meanwhile, the background noise is much stronger. In addition, the reproducibility is much lower than that of rGO film.



Figure S9. Mass spectra of 5 ng OCDD on (a) silica particles and (b) silica particles modified with ¹⁰ carbon black.

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