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Reduced graphene oxide films used as matrix of MALDI-TOF-MS for detection of octachlorodibenzo-p-dioxin†

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A reduced graphene oxide (rGO) film was used as the matrix in the matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) for the detection of octachlorodibenzo-p-dioxin (OCDD) with a detection weight as low as 500 pg.

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS)^{1–3} is an important tool for analyzing and characterizing a wide range of materials,^{3–8} including synthetic polymers and biomolecules. In particular, the mass spectra of biomolecules, such as proteins, peptides^{3,5,8} and nucleic acids,⁶ have been used to characterize their structural information. However, less attention has been paid to the detection of environmentally toxic molecules (*e.g.* dioxins) using MALDI-TOF-MS, which could offer higher accuracy and sensitivity and will implement measures against the occurrence of these toxic molecules in the environment.

Polychlorinated dibenzodioxins, or simply dioxins, are well-known human carcinogens and stable pollutants in air, water, soil and food chains. They are a family of compounds comprised of two benzene rings joined together by two oxygen bridges bearing zero to eight chlorine atoms around the two rings. Their toxicity strongly depends on the number and position of the chlorine atoms. Therefore, it is of great necessity to detect dioxins with higher accuracy and sensitivity. To date, there is no report on the use of MALDI-TOF-MS for the analysis and detection of dioxins, although some other methods, *e.g.* GC/MS, have been carried out to do so.^{9–11} One possible reason is the lack of a suitable matrix. The conventionally used matrix, such as 2,5-dihydroxybenzoic acid (DHB), is not suitable for dioxin detection.

Graphene has attracted increasing interest since its discovery in 2004.^{12,13} Recently, the derivatives of graphene, graphene oxide (GO) and reduced graphene oxide (rGO), have been widely studied in various applications,^{14–30} since GO and rGO are easily produced in large amounts by using chemical methods.^{20,23}

In this communication, the rGO film, prepared by spin-coating GO solution on SiO₂ substrate and then reduced with

hydrazine vapor,^{21,22} was used as the matrix of MALDI-TOF-MS for the analysis of octachlorodibenzo-p-dioxin (OCDD), a dioxin with eight chlorine atoms. The rGO film, composed of π -conjugated networks, not only can adsorb the analytes (*i.e.* OCDD), but also can absorb the energy from the laser radiation, conduct heat, and transfer energy and charges (*i.e.* electrons) to analytes for the desorption/ionization process. The highly efficient desorption/ionization was obtained on rGO film without any requirement for locating the “sweet spots”, which are required for the conventional organic matrices. This simplifies the sample preparation. In comparison, other matrices, including rGO powder, graphite powder, activated carbon powder, single-walled carbon nanotubes (SWCNTs), and silica particles, were also used for the analysis of OCDD (see the ESI†), which all showed the lower sensitivity compared to that obtained by using rGO film as a matrix.

Fig. 1 shows the spectra of OCDD by using rGO film as a matrix. 5 ng and 500 pg of OCDD can be easily detected (Fig. 1a and b). Note that no peaks of deprotonated species [M–H][–] were detected. Instead, the dominant peaks for OCDD at m/z 419.6, 421.6, 423.6, and 425.6 were shown. These peaks are attributed to the fragmented species [M–Cl][–], with the isotopic multiplet of Cl well resolved. As such, the ionization of OCDD is proposed as:

where M represents the analyte OCDD, which captures an electron and releases a chloro radical.

Other commonly used organic matrices, such as 2,5-dihydroxybenzoic acid (DHB), α -cyano-4-hydroxycinnamic acid

Fig. 1 Mass spectra of OCDD with (a) 5 ng, (b) 500 pg, and (c) 50 pg adsorbed on rGO film. Insets: (left) molecular structure of OCDD; (right) amplified mass spectrum of (b).

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Fig. 2 Mass spectra of (a) 10 ng, (b) 1 ng, (c) 500 pg, and (d) 100 pg OCDD adsorbed onto 24 ng rGO powder.

(CHCA) and sinapic acid (SA), have also been employed for the detection of OCDD, but no signals were observed. Therefore, in our experiments, none of these conventionally used organic matrices can be used for detection of OCDD.

The effective desorption/ionization is reasonable if the structure of the rGO film is considered. The rGO sheet is composed of π -conjugated networks, which could absorb energy from UV laser radiation, and transfer energy to analytes to assist the desorption/ionization.³¹ In addition, the abundant electrons in the π -conjugated system can be transferred to analytes to assist the ionization of analytes as proposed (eqn (1)). It is worth mentioning that the residual oxygenated functional groups may also play an important role in the desorption/ionization process because the pure graphite powder shows a lower sensitivity in the detection of OCDD (see the ESI†). It is supposed that the released radical $\text{Cl}^\bullet$ is easily captured by the adjacent residual hydroxyl or carbonyl or carboxyl groups, which are present on the rGO films. However, no such oxygenated functional groups exist on graphite to assist such a capture process. Besides, the continuous rGO film is advantageous since the laser energy is easily captured and conducted through the rGO film.³¹

Besides rGO film, rGO powder, as a solid-phase extraction agent and matrix, was also used for the detection of OCDD (see the ESI†). Fig. 2 shows the mass spectra of different quantities of OCDD on rGO powder. 10 ng and 1 ng of

Fig. 3 Mass spectra of 500 pg OCDD adsorbed on (a) rGO film and (b) rGO powder. Inset: amplified spectrum of (a).

OCDD were easily detected. However, if the quantity of OCDD is < 500 pg, the signal became weak and the signal-to-noise ratio decreased significantly. Fig. 3a and b show the spectra of 500 pg of OCDD by using rGO film and rGO powder as matrices, respectively, which proved that the efficiency of desorption/ionization on rGO film is much better than that of the rGO powder. This is attributed to the fact that the rGO powder is not well connected and thus the ability to absorb laser energy is decreased.

Another comparison study was also carried out by using other materials, such as the natural graphite powder, activated carbon powder, SWCNTs and silica particles, as matrices for the detection of OCDD (see the ESI†). These materials have been employed as matrices for analysis of other molecules.^{32–36} However, our experimental results showed that these materials did not act as good matrices for OCDD, as compared with rGO film, with either a higher detection weight or a lower signal-to-noise ratio (see the detailed experiments in the ESI†).

In summary, the ability of rGO film to act as a matrix in MALDI-TOF-MS for OCDD detection was demonstrated in this study. The rGO film is so far the best matrix for the OCDD detection as compared with other matrices used in our experiments. As little as 500 pg of OCDD was detected in our experiments. The high sensitivity attained with rGO film is attributed to the distinct structure of rGO, which is comprised of π -conjugated networks and could facilitate the desorption/ionization process. Therefore, the rGO film could be a potential matrix for detection of other materials including biomaterials.

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