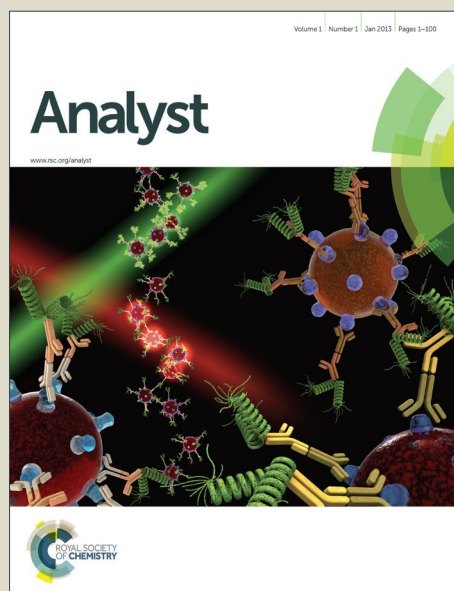


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ARTICLE TYPE

Magnetic graphene composites as both adsorbent for sample enrichment and MALDI-TOF MS matrix for the detection of nitropolycyclic aromatic hydrocarbons in PM_{2.5}

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A simple and rapid method that uses the synthesized magnetic graphene composites as both adsorbent for enrichment and matrix in MALDI-TOF MS analysis was developed for the detection of nitropolycyclic aromatic hydrocarbons (nitro-PAHs) in PM_{2.5} samples. Three nitro-PAHs were detected down to sub pg•μL⁻¹ level based on the calculation from instrumental signal-to-noise better than 3, which shows the feasibility of using new material in MALDI-TOF MS as a potential powerful analytical approach for the analysis of nitro-PAHs in PM_{2.5} samples.

1 Introduction

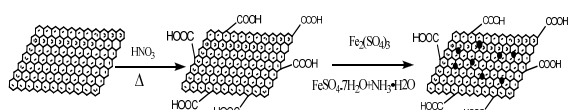
Nitropolycyclic aromatic hydrocarbons (nitro-PAHs) are a class of potentially mutagenic and carcinogenic environmental pollutants.¹⁻² Atmospheric nitro-PAHs compounds are mainly emitted from fossil fuel combustions such as automobile exhausts and coal-fired power plants.^{3, 4} In addition to the direct emission sources, some nitro-PAHs such as 2-nitrofluoranthene and 2-nitropyrene can also be formed from the photochemical reactions of PAHs in ambient air.^{5, 6} Due to their relatively low volatilities, nitro-PAHs are ready to partition onto the fine particulates (PM_{2.5}) and gradually accumulate in the aerosol phase. This could cause adverse effect on human health because PM_{2.5} particles can easily penetrate deep into human lung and bloodstream. Thus, development of rapid, sensitive and selective methods for the determination of nitro-PAHs in PM_{2.5} particles is becoming increasingly important. Methods of chromatography and mass spectrometry have been reported for the analysis of nitro-PAHs in air samples, including gas chromatography with electron capture detection (GC-ECD)⁷ and mass spectrometry under negative ionization mode (GC-NCI-MS)⁷⁻¹¹ as well as high performance liquid chromatography (HPLC) with electrochemical detection¹² and mass spectrometry (LC-MS).¹³ However, the above instrumental analyses required intensive sample pretreatment. Matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOFMS) has become an indispensable tool for the analysis of large molecules since its introduction in 1990s.^{14, 15} The interference of matrix ions makes the characterization of small molecules obscured and difficult. To overcome this problem, various sample-supporting materials such as porous silicon,¹⁶⁻¹⁹ titania microparticles and nanoparticles,²⁰⁻²² polymer,²³ surfactant suppressed matrix²⁴ and carbon materials²⁵⁻²⁹ were applied in

MALDI-TOF MS analysis of small molecules.

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With the excellent optical and electrical properties,^{30, 31} graphene is considered as a prominent material in energy absorption, storage and transfer³², which makes it an excellent MALDI matrix. Analysis of small molecules including peptides, amino acids, fatty acids, as well as nucleosides and nucleotides by using graphene matrix has been reported.³³⁻³⁶ With the relatively high tolerance to interference, the method was employed with simple sample pretreatment or even no pretreatment. The graphene matrix-based MALDI-TOF MS might also be applied for rapid analysis of PAHs and nitro-PAHs in environmental samples such as PM_{2.5}. However, because the level of nitro-PAHs in PM_{2.5} is very low, sample extraction is necessary for the purpose of analyte enrichment. With the unique two-dimensional plate-like structure and very high specific surface area (2630 m²•g⁻¹), graphene is a prominent material as an adsorbent with high loading capacity.³⁷ On the other hand, graphene also has a large delocalized Pi-electron system that endues the material with a strong affinity for carbon-based ring structures. Thus, graphene may be an ideal enrichment material for nitro-PAHs. However, because graphene is a one-atom-thick layer sheet, it is difficult to completely separate the material from sample solution after the extraction even by using high-speed centrifugation. In order to improve the enrichment, magnetic graphene was synthesized and used given its good separation

capability with the aid of external magnetic field. More importantly, with the simple monolayer structure and unique electronic properties, magnetic graphene did not show interference for its use as the matrix in MALDI-TOF MS analysis. A material of magnetic oxidized graphene composites (MAOG) was successfully synthesized through a two-step reaction (Scheme 1). Graphene was first acid-oxidized using previously described procedures.³⁸ The acid-oxidized graphene (AOG) was further magnetized. The HNO₃-treated graphene possesses carboxylic groups on the outer surface so that it can easily combine with Fe₃O₄ spheres. The synthesized composites served as both absorbent in the pretreatment of nitro-PAHs samples and matrix in MALDI-TOF MS analysis. This not only simplified the enrichment process with magnetic separation, but also eliminated the interferences caused by conventional matrices. Nitro-PAHs were detected without interference from non-substituted PAHs by MALDI-TOF MS in negative ionization mode. The method was successfully applied in the analysis of nitro-PAHs in PM_{2.5} samples.



Scheme 1. Synthetic route of MAOG.

2 Experimental

2.1 Chemicals and reagents

Graphene was purchased from Nanjing XFNANO Materials TECH Co., Ltd. All the authentic standard compounds such as 1-nitropyrene, 2-nitrofluorene and 9-nitroanthracene were from Accustandard, Inc. USA. Stock solutions of nitro-PAHs standards were prepared at concentrations of 1.0 ng·μL⁻¹ in dichloromethane (DCM). Iron (II) sulfate heptahydrate and Iron (III) sulfate hydrate were purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd. Distilled water was purified by a Milli-Q system (Milford, MA, USA).

MAOG was synthesized by two steps (Scheme 1). Graphene was first acid-oxidized according to procedures described previously³³. Briefly, graphene (200 mg) was dispersed into 20 mL 2M HNO₃ at 105 °C with magnetic stirring for 7 hours. After the reaction, the graphene treated by HNO₃ (AOG) was collected upon the water wash for five times and then freeze-dried. AOG possess some carboxylic groups on the outer surface. The carboxylic group can easily combine with Fe₃O₄ spheres. The acid-oxidized graphene was further magnetized. The dried pretreated graphene (60 mg), Fe₂(SO₄)₃ (30 mg) and FeSO₄·7H₂O (21.5 mg) were dispersed into 20 mL water and sonicated for 10 min. The mixture was preheated to 80°C prior to the coprecipitation reaction. Subsequently, 1 mL of ammonia solution (28 wt%) was quickly added and vigorously stirred for 1 hour. The produced magnetic acid-graphene composites were collected with the help of a magnet and thoroughly washed five times with deionized water and freeze-dried.

2.2 Enrichment of nitro-PAHs with magnetic graphene composites as adsorbent and MALDI matrix

Standard solution of 10 pg·μL⁻¹ nitro-PAHs was prepared by diluting standard stock solutions with DCM/ACN (1:1, v/v). Three milligrams of MAOG was suspended in 1.0 mL of water/ethanol (1:1, v/v) mixture and sonicated for 30 min. Then 10 μL of the suspension was pipetted immediately into 200 μL of 10 pg·μL⁻¹ nitro-PAHs standard solutions. The mixture was then vibrated for 30 min and magnetically separated with an external magnetic field. After the magnetic separation, the MAOG portion was added into 10 μL of water/ethanol (1:1, v/v). Approximately 1.0 μL of the magnetic graphene suspension was then spotted on the MALDI plate. After the solvent was evaporated, the sample was analyzed by MALDI-TOF MS. The obtained peak intensity of each nitro-PAHs in the enrichment samples was compared with that from the analysis of standard solution at the corresponding level in order to measure the enrichment efficiency.

2.3 Instrumentation

Transmission electron microscopy (TEM) images were taken on a Tecnai G2 20 S-TWIN Transmission Electron Microscope operated at 200 kV. Scanning electronic microscope (SEM) images were recorded on a LEO1530VP electron microscope (Germany) operated at 20 kV. Fourier transform infrared spectra (FTIR) were collected on a Nicolet magna 550 series II spectrophotometer using KBr pellets (USA). MALDI-TOF MS analysis was performed on a Bruker Autoflex II mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen laser (337 nm wavelength; 3 ns pulse width). The laser power energy was adjusted between 0% and 100% to provide the laser pulse energy between 93.8 and 121.8 μJ. One microliter of each of the standard solution containing nitro-PAHs at 10 pg·μL⁻¹, the recovery testing sample, or the PM_{2.5} sample extract was loaded on the MALDI plate together with 3 μg of MAOG. The MALDI-TOF MS measurements were performed in negative ionization mode. Each mass spectrum was acquired as an average of 300 laser shots. Under the ample conditions, the nitro-PAHs were also loaded on the MALDI plate and analyzed without using any matrix.

2.4 Sampling and pretreatment of PM_{2.5} sample

PM_{2.5} sample was collected on the rooftop of environmental science and engineering research center in Shanxi University (about 25 m above the ground) using an active sampler (Thermo Anderson, USA) at a flow rate of 1.13 m³·min⁻¹. This site is located approximately 300 m away from a major roadway. There are no obvious industrial pollution sources around. Thus, the sampling site can be considered as a general urban site in Taiyuan. PM_{2.5} sample was collected onto a quartz fiber filter (203×254 mm, Whatman, PMA, GE Healthcare Life Sciences, UK) for 24 hours on January 20, 2013.

The whole PM_{2.5} sample filter was cut into 1 cm × 1 cm size, placed in a 100 mL beaker and extracted twice with 50 mL of DCM under ultrasonic assistance. The extracts were combined and dried under a pure stream of N₂. Then the residue was dispersed into 200 μL of DCM/ACN (1:1, v/v). Three milligrams of MAOG was suspended in 1 mL of water/ethanol (1:1, v/v) mixture and sonicated for 30 min. An aliquot of 10 μL suspension of MAOG was applied for the enrichment of nitro-PAHs in the sample extract. The enriched nitro-PAHs were analyzed using MALDI-TOFMS with MAOG as matrix.

3 Results and Discussion

In this work, MAOG was synthesized as the enrichment material given its large surface area, large delocalized π -electron system and carboxyl active group. This structure is very easy to be attached the carbon-based ring structures such as PAHs and nitro-PAHs and the enrichment process will be greatly simplified by the magnetic separation. Besides, graphene composites can also directly serve as a matrix of MALDI-TOF MS analysis without interferences caused by matrices ions.

3.1 Characterization of MAOG

The synthesized materials were characterized using different techniques, including infrared spectroscopy and electron microscopy (SEM and TEM). Figure 1 shows the FTIR spectra of graphene (G), AOG and MAOG. Graphene did not show any significant peaks in the FTIR spectrum. For AOG and MAOG, peaks of 1622 cm^{-1} and 3450 cm^{-1} were observed, indicating that the oxidation occurred in G sheets. For MAOG, another intense signal was observed at 571 cm^{-1} , which was assigned to Fe-O stretching of Fe_3O_4 , indicating that the magnetic particles were successfully composed with AOG.

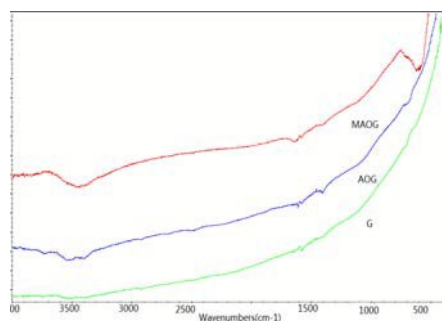


Fig. 1 FTIR spectra of G, AOG and MAOG.

The morphology of MAOG composites was characterized by SEM and TEM (Fig. 2). Many wrinkled textures corresponding to the folded regions of AOG and MAOG were observed with a nearly transparent flake-like structure with characteristic crumpled silk waves and single-layer nature. Compared to AOG, the SEM and TEM images (Fig. 2b and 2d) of MAOG showed many magnetic beads on the surface of graphene with one-atom-thick layer sheets, which indicated the successful combination of Fe_3O_4 on the surface of mild oxidized graphene.

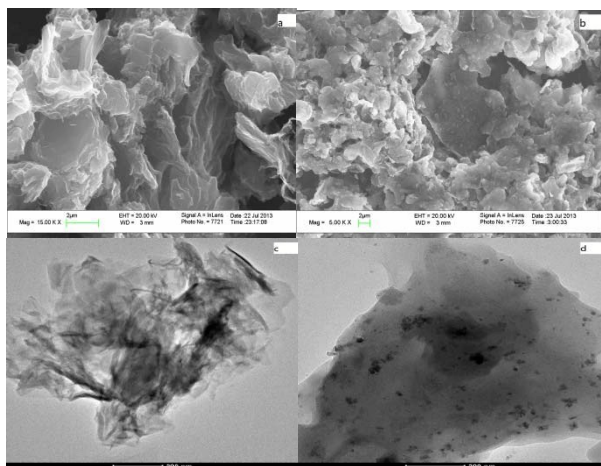


Fig. 2 SEM images of AOG (a) and MAOG (b) as well as TEM images of AOG (c) and MAOG (d).

3.2 Enrichment of nitro-PAHs with magnetic graphene composites as the adsorbents

The synthesized MAOG was employed as adsorbent for the enrichment of three nitro-PAHs, namely 1-nitropyrene, 2-nitrofluorene and 9-nitroanthracene. These three nitro-PAHs were selected for study not only due to their availability but also because they are common nitro-PAHs existing in ambient environment. The solvent mixture of DCM/ACN (1:1, v/v) was selected because it not only ensured good solubility of nitro-PAHs but also provided excellent dispersity of MAOG, which was greatly beneficial for good enrichment efficiency. Other solvents such as DCM alone and a mixture of DCM/THF (1:1, v/v) were also tested. Although the solvents could provide good solubility for the analytes, the dispersity of MAOG was poor in these solvents. Furthermore, when using the DCM/ACN solvent mixture, the magnetic separation was simple and rapid. The separated nitro-PAHs-containing MAOG was then directly analyzed by MALDI-TOF MS.

3.3 MALDI-TOF MS analysis of nitro-PAHs with magnetic graphene composites directly as the matrix

Because nitro group in the nitro-PAHs has much greater electron affinities than the non-substituted PAHs, negative ions of nitro-PAHs might be more easily acquired in MALDI-TOF MS analysis with negative ionization mode. Analysis of the compounds was performed without using any matrix for the examination on whether the nitro-PAHs could be desorbed by laser or ionized. No peak of nitro-PAHs was detected when no matrix was used. The nitro-PAHs were then analyzed using MALDI-TOFMS with MAOG as the matrix. The method was specific for nitro-PAHs because PAHs were not detectable under these conditions. The mass spectra of three nitro-PAHs obtained from the analysis of the standard solution are shown in Figure 3. For 1-nitropyrene and 9-nitroanthracene, $[\text{M}-\text{NO}]^-$ ion was the base peak, and a minor molecular anion $[\text{M}]^-$ peak was also observed (Fig. 3a and b). For 2-nitrofluorene, $[\text{M}-\text{H}]^-$ ion peak was detected as the base peak, along with a minor peak of $[\text{M}-\text{H}+\text{O}]^-$ (Fig. 3c). The formation of $[\text{M}-\text{H}+\text{O}]^-$ in the negative ion MALDI-TOF MS of nitro-PAHs may be resulted from the ion-molecule reaction, which is between ions derived from the nitro compound and the neutral molecules of the same compound.³⁹ The detection of the base peak of $[\text{M}-\text{H}]^-$ ion for 2-nitrofluorene may be due to its ability of deprotonation. Figure 4a shows the spectrum from the analysis of standard mixture containing the nitro-PAHs at $10\text{ pg}\cdot\mu\text{L}^{-1}$ with detection of the above characteristic ions. The exact masses from the analysis of individual standard compound and mixture of the three well matched the corresponding theoretical values with an error of less than 10 ppm. Formation of $[\text{M}]^-$, $[\text{M}-\text{H}]^-$, and $[\text{M}-\text{NO}]^-$ ions of nitro-PAHs from the negative LDI-TOF MS analysis was previously reported and discussed.⁴⁰

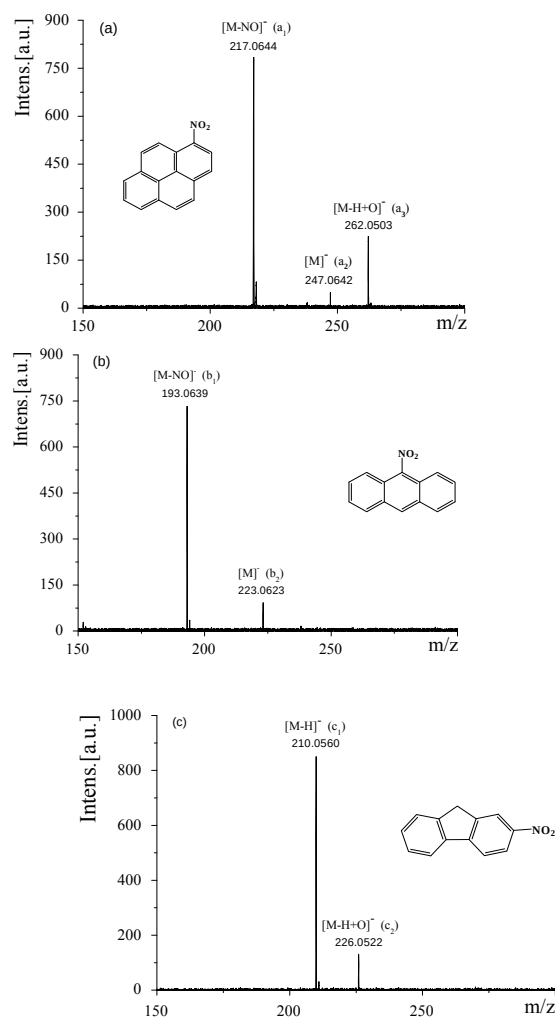


Fig. 3 MALDI-TOF MS spectra of three nitro-PAHs after using MAOG as the enrichment absorbent and MALDI matrix in negative ionization mode.

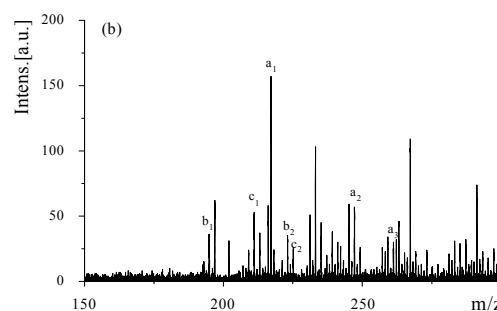
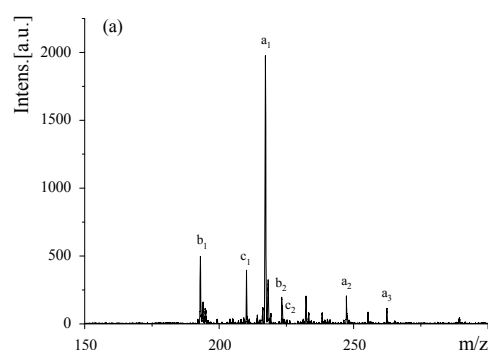


Fig. 4 Mass spectra from the analysis of mixture of the three nitro-PAHs (a) and PM_{2.5} sample with the detection of the three nitro-PAHs (b). Comparison of the measured masses of the characteristic ions with the corresponding theoretical values of the 3 nitro-PAHs in the PM_{2.5} sample is listed in Table 1.

Table 1. Comparison of the measured masses of characteristic ions with the corresponding theoretical values of the 3 nitro-PAHs detected in PM_{2.5} sample.

Nitro-PAHs	Peak ion	Characteristic ion	Measurement	Theoretical value	Error (ppm)
1-nitropyrene	a ₁	[M-NO] ⁻	217.0644	217.0653	4.15
	a ₂	[M] ⁻	247.0642	247.0633	3.64
	a ₃	[M+O-H] ⁻	262.0503	262.0504	0.38
9-nitroanthracene	b ₁	[M-NO] ⁻	193.0639	193.0653	7.25
	b ₂	[M] ⁻	223.0623	223.0633	4.48
2-nitrofluorene	c ₁	[M-H] ⁻	210.0560	210.0555	2.38
	c ₂	[M+O-H] ⁻	226.0522	226.0504	7.96

The enrichment efficiency and detection limit were examined by performing 3 sample enrichments with triplicated MALDI-TOF MS analysis. The averaged intensity of the base ion peak of each nitro-PAHs in the extract was compared with that in standard analysis without the enrichment in order to estimate the recovery. The recovery of using 30 µg MAOG for enrichment of 200 µL solution containing nitro-PAHs at 10 pg·µL⁻¹ was 70±12% (n=9). Moreover, the MAOG could be used for multiple times with the similar recovery. It should be noted, however, that the enrichment efficiency was estimated, given the significant variation during MALDI sample loading and TOFMS analysis. More accurate determination should be performed when isotope labeled internal standard would be available. The detection limit of instrument with S/N of 3 was estimated to be 1–2 pg. The method could be used for the analysis of nitro-PAHs at sub pg·µL⁻¹ levels. The method detection limit, however, might be seriously affected when real environmental sample would be analyzed because significant background noise might exist and no chromatographic separation was applied.

3.4 Application of the method to the real samples of PM_{2.5}

The developed method was applied for the analysis of the nitro-PAHs in PM_{2.5} sample to demonstrate its feasibility for real sample analysis. The details of PM_{2.5} sample collection were described in Section 2.4. The sample extracts were analyzed using MALDI-TOFMS with MAOG as matrix. The characteristic peaks with the exact masses matching 1-nitropyrene, 2-nitrofluorene, and 9-nitroanthracene were detected (Figure 4b). Although numerous peaks were observed, the detected ion peaks were assigned to nitro-PAHs in the PM_{2.5} sample with the

measured masses matched well to the corresponding theoretical values with an error of less than 10 ppm (Table 1). The detection of the 3 nitro-PAHs was confirmed with the GC-NCI-MS analysis by using the method reported previously.¹¹ The averaged levels of 1-nitropyrene, 2-nitrofluorene and 9-nitroanthracene in the PM_{2.5} samples were determined as 0.309 ng/m³, 0.118 ng/m³, and 0.019 ng/m³, respectively. Given their levels in the sample extract around 10-200 pg·μL⁻¹, the 3 nitro-PAHs were easily detected in the same sample extract by the developed MALDI-TOF MS method. Other potentially existing nitro-PAHs were not targeted due to the lack of authentic standards for comparison. It should be noted that the detected ions referred to isomers of each corresponding nitro-PAH compound because the isomers with the same characteristic ion were not separated. Furthermore, the levels of the detected nitro-PAHs could not be accurately quantified under the current conditions. The main objective of this study was method development for the detection of nitro-PAHs by using MAOG as adsorbent for enrichment and matrix for MALDI-TOF MS analysis. The analytical data might be used to compare nitro-PAHs contamination from similar sources.

4 Conclusions

MAOG was successfully synthesized with a simple two-step reaction and applied as both adsorbent for the enrichment of three common nitro-PAHs and matrix for MALDI-TOF MS analysis. Results show that MAOG can efficiently enrich the nitro-PAHs and separate them from environmental sample extract with the aid of external magnetic field. The method with negative ion MALDI-TOF MS was specific for nitro-PAHs because PAHs were not detectable under these experimental conditions. The outcome of this study provides a new approach for rapid, simple and selective detection of nitro-PAHs. Although only three nitro-PAHs were determined in this study, the developed method can definitely be extended to other nitro-PAHs. The current method development, however, has a primary limitation in quantitative analysis of the nitro-PAHs, which should be investigated when isotope-labelled internal standard of the corresponding nitro-PAHs would be available. Further investigation should also be conducted on the enrichment efficiency of MAOG when quantitative method would be available. Nevertheless, this study described a successful method development for the detection of nitro-PAHs using the synthesized MAOG as both adsorbent for enrichment and matrix for MALDI-TOF MS analysis, and provided evidence of detecting three nitro-PAHs in the PM_{2.5} sample. This study also provided an example of using new material in MALDI-TOF MS as a potential powerful analytical approach for the analysis of small molecules in environmental samples.

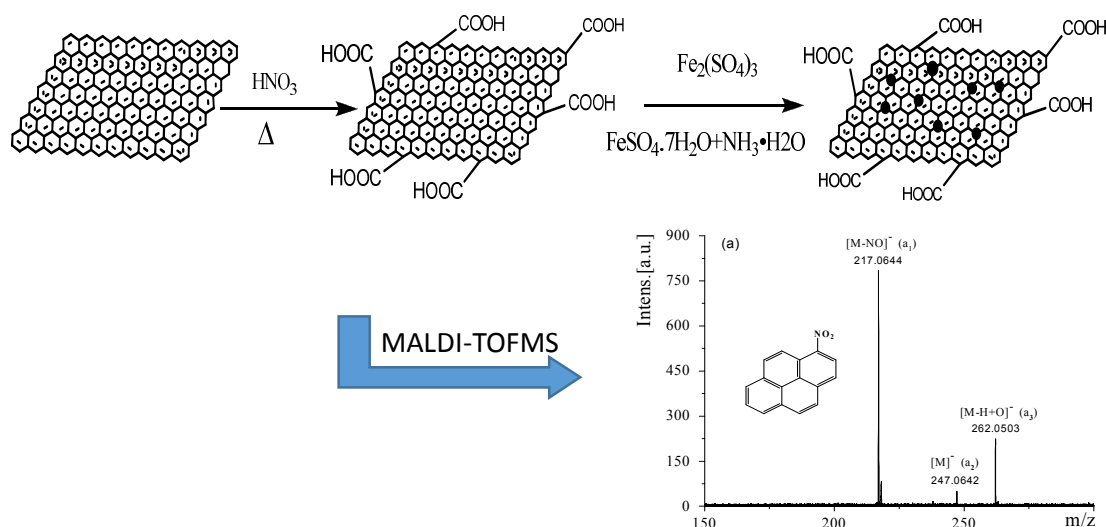
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Magnetic graphene composites were synthesized and applied as both adsorbent for sample enrichment and matrix for MALDI-TOFMS detection of 3 nitropolycyclic aromatic hydrocarbons in $\text{PM}_{2.5}$ samples.