Talanta 114 (2013) 54–59

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Graphene matrix for signal enhancement in ambient plasma assisted laser desorption ionization mass spectrometry

Cuilan Chang, Xianjiang Li, Yu Bai*, Gege Xu, Baosheng Feng, Yiping Liao, Huwei Liu*

Beijing National Laboratory for Molecular Sciences, the Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Institute of Analytical Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:
Received 14 December 2012
Received in revised form
26 March 2013
Accepted 4 April 2013
Available online 12 April 2013

Keywords:
Ambient PALDI-MS
Graphene
α-cyano-4-hydroxycinnamic acid
Graphene oxide
Signal enhancement

ABSTRACT

In this work, the signal intensity of ambient plasma assisted laser desorption ionization mass spectrometry (PALDI-MS) was significantly increased with graphene as matrix. The graphene functions as a substrate to trap analytes, absorb energy from the visible laser irradiation and transfer energy to the analytes to facilitate the laser desorption process. The desorbed analytes are further ionized by helium plasma and analyzed by MS. Compared with a traditional organic matrix, α-cyano-4-hydroxycinnamic acid (CHCA), graphene exhibited much higher desorption efficiency for most of the compounds benefitting from the strong optical absorption at 532 nm. The performance has been confirmed by the facile analysis of more than forty compounds with various structures. Additionally, this method was successfully applied to distinguish three kinds of Chinese tea leaves by detecting the endogenous caffeine and theanine, which proved the utility, facility and convenience of this method for rapid screening of main components in real samples.

1. Introduction

Direct analysis in real time mass spectrometry (DART-MS) [1], which is operated in the open air conditions and requires minimal or no sample preparation, is one of the most widely used ambient mass spectrometry. Helium or nitrogen metastable plasma is created by high-voltage glow discharging. Then the heated plasma blows to the sample surface, and the protons are transferred to analytes through the reactive species in the ambient atmosphere, such as water clusters [1,2]. DART-MS could provide a rapid and direct way to analyze many kinds of samples, such as direct analysis of activity assays from live samples [3,4], fast screening of target compounds in real samples [5–7], obtaining evidence of sexual assaults [8], reaction monitoring in drug discoveries [9], quantitative detections of warfare agents [10], and efficient analysis of environmental samples after stir bar absorptive extraction [11]. Since DART is a plasma-based ambient ionization source, the desorption area depends on the plasma stream with several millimeters in diameter, which prevents its utilization for mass spectrometry imaging. The improvement of the spatial resolution can be achieved by using laser desorption and plasma assisted ionization process [12]. Based on these, our lab constructed an ambient plasma assisted laser desorption ionization mass spectrometry (PALDI-MS) system [13], and the previous results indicated that using a proper matrix to enhance the laser desorption process will definitely improve the signal intensity and detection sensitivity [14]. However, little attention has been paid to look for such matrices in laser based ambient MS [14–16].

Graphene has attracted increasing interests because of its outstanding properties since Novoselov and Geim et al. succeeded in preparing single-layer graphene in lab by simple mechanical exfoliation in 2004 [17]. This single atom thick and two-dimensional nanomaterial possesses large surface area (2630 m^2/g), excellent optical absorption and super electrical properties. With the inherent superiorities, graphene was considered as a prominent material in energy absorption, storage and transfer [18–21]. Recently, graphene-based nanomaterials have been successfully used as matrices in MALDI-ToF-MS for the detections of small molecules without matrix interferences [22–27]. So far, there is no report on the matrix effects of graphene in laser desorption process under ambient conditions.

In this study, graphene was used as the matrix to increase the signal intensity of PALDI-MS. Since graphene has large surface area and strong optical absorption across the visible range, it could not only adsorb the analyte molecules, but also act as an excellent medium to transfer the energy of laser irradiation to the analytes. The efficient energy absorption and transfer facilitate the desorption process, thus enhancing the signal intensity of MS. Owing to its superiority in interaction with analytes and visible laser absorption, homogeneous sample layer can be formed after the addition of graphene, and a higher desorption efficiency for most of the compounds has been presented when compared with a traditional matrix CHCA. In addition, the matrix effects of graphene oxide have also been investigated because it has similar π-conjugated structure with graphene. Graphene oxide exhibited considerable signal enhancement for PALDI-MS as

* Corresponding authors. Tel.: +86 10 62754976; fax: +86 10 62751708.
E-mail addresses: yu.bai@pku.edu.cn (Y. Bai), hwliu@pku.edu.cn (H. Liu).

0039-9140/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.talanta.2013.04.007

well, but not as high as graphene, which may result from its polar moieties. The performance was confirmed by the facile analysis of more than forty compounds with various structures, which demonstrated that graphene was a more general and effective matrix for ambient PALDI-MS. Finally, we used this method to analyze three kinds of Chinese teas and successfully distinguished them by the different contents of their endogenous caffeine and theanine, which proved the applicability of this method for real samples.

2. Experimental

2.1. Chemicals and reagents

Graphene aqueous suspension (0.5 mg/mL) and graphene oxide powder were obtained from Nanjing XFNANO Materials Tech Co., Ltd. (Jiangsu, China). CHCA was purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade methanol and purified water were obtained from Dikma Technologies Inc. (CA, USA) and Hangzhou Wahaha Group Co., Ltd. (Zhejiang, China), respectively. Model compounds without special declaration were all obtained from commercial source, and they were used in the experiments without further purification.

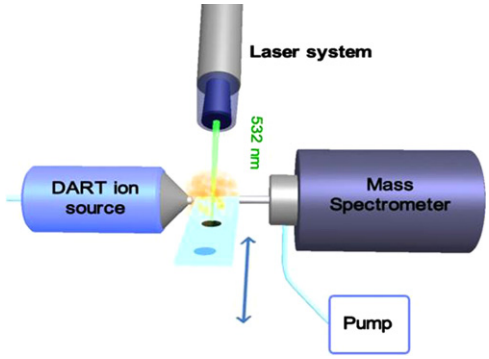

Fig. 1. Schematic illustration of the plasma assisted laser desorption ionization mass spectrometry (PALDI-MS).

2.2. Sample preparation for analysis

All of the model compounds without additional comments were dissolved in methanol and prepared at the concentration of 1.0 mg/mL. Graphene oxide powder (3.0 mg) was dispersed in 6 mL water and sonicated for 5 min to obtain homogeneous graphene oxide suspension at the concentration of 0.5 mg/mL.

Graphene and graphene oxide suspensions were sonicated for 3 min before use. Sample solutions were prepared by mixing the analyte solutions with water, graphene, CHCA or graphene oxide suspensions (1:1, v/v), respectively. The final concentration of the model compounds were 0.5 mg/mL. After sonication for 3 min, 5.0 μL solutions were dropped onto the sample plate and dried in the open air for further analysis.

2.3. Apparatus

The schematic illustration of the setup was shown in Fig. 1. The PALDI-MS system successfully integrated the visible laser ablation, the excited plasma from direct analysis in real time (DART) and Time-of-Flight MS (ToF MS). The DART®-SVP ion source (IonSense, Saugus, MA, USA) was coupled to an Agilent MSD ToF MS (Agilent Technologies, Palo Alto, CA, USA) after removing the Agilent dual electrospray ionization source. The pulsed Nd:YAG laser (Lai Yin Opto-Electronics Technology, Beijing, China) was operated at 532 nm

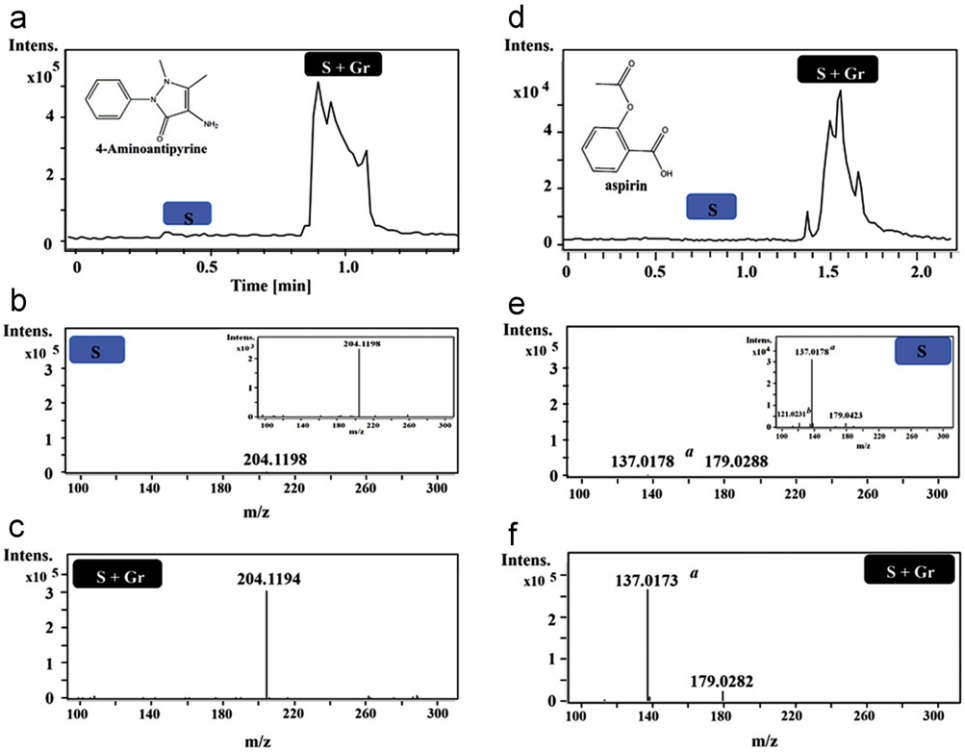

Fig. 2. Mass spectra of 4-aminoantipyrine and aspirin under 532 nm of laser without/with graphene as the matrix. (a) EIC of 4-aminoantipyrine (*m*/*z*, 204.1131) in positive ion mode; (b) averaged mass spectrum of 4-aminoantipyrine without matrix (inlet is the amplified average mass spectrum); (c) averaged mass spectrum of 4-aminoantipyrine with graphene as the matrix; (d) EIC of aspirin (*m*/*z*, 137.0178) in negative ion mode; (e) averaged mass spectrum of aspirin without matrix (inlet is the amplified average mass spectrum); (f) averaged mass spectrum of aspirin with graphene as the matrix.