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A homogeneous carbon nanosphere film-spot: For highly efficient laser desorption/ionization of small biomolecules

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ABSTRACT

In this work, a novel strategy for highly efficient detection of small molecules with a homogeneous carbon nanosphere film-spot (HCNFs) was carried out for the first time by negative surface-assisted laser desorption/ionization time-of-flight mass spectroscopy (SALDI-TOF MS). The HCNFs was fabricated by monolayer oxidized carbon nanospheres (OCS) self-assembling on laser desorption/ionization (LDI) target. With the HCNFs, no background interference and exclusive deprotonated ($[M-H]^-$) peaks of analytes were obtained for a wide range of small biomolecules including fatty acids, amino acids, nucleobases, traditional Chinese medicines, and anti-cancer drugs in the negative SALDI-TOF MS. Comparing with other carbon-based matrices as well as the organic matrix, the monolayer OCS film exhibited various advantages including fewer interfering fragments, stronger signal intensities, and higher detection sensitivity. Moreover, with the improved spotting homogeneity of the HCNFs, "sweet-spot" searching on LDI target was avoided and good reproducibility was obtained in the LDI-TOF MS analysis. This study is expanding the application of carbon nanospheres and providing a promising approach for rapid analysis of small molecules with none-interference and good reproducibility.

1. Introduction

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), as a soft ionization mass spectrometry technique, has become a powerful platform for the detection of peptides, proteins, and metabolites [1–4]. However, the severe background interference in the low mass region (m/z < 500 Da) suffered from the traditional organic matrices of MALDI-TOF MS makes this high-throughput tool powerless in the analysis of small molecules [5]. Moreover, the sweet-spot phenomenon resulting from the heterogeneity of matrix-analytes crystallization on a LDI target also leads to poor shot-to-shot reproducibility of LDI-TOF MS [6].

To overcome these problems, the surface-assisted laser desorption/ionization time-of-flight mass spectrometry (SALDI-TOF MS) using nanostructured substrates or nanomaterials as matrices instead of the conventional organic matrices in MALDI-TOF MS has been developed [7,8]. Up to now, nanostructured substrates or nanomaterials including porous silicon [9,10], HgTe nanostructures [11], indium tin oxide slide [12], metallic nanomaterials (gold [13–18], titanium dioxide [19,20], metal organic frameworks [21]) and carbon-based materials have been applied as matrices for SALDI-TOF MS. Among them, the carbon-based materials including fullerenes, carbon nanotubes (CNTs), graphene, carbon nanodots, nanoporous carbon, and their derivative forms have attracted particular attention owing to their high conductivity, great light absorption and excellent energy transfer efficiency for SALDI [22–28]. Yet, the low solubility and poor dispersibility of pristine carbon-based matrices always lead to unsatisfactory reproducibility of SALDI-TOF MS [23,29]. Great efforts have been made to improve the solubility and dispersibility of these materials by oxidation or hydrophilic modification progress [29–32]. Besides, researchers try to fabricate carbon-based films (i.e., graphene oxide (GO)/CNTs double layer [33,34], gold/GO hybrid film [35], and polystyrene/CNTs hybrid film [36]) on LDI plate, attempting to improve the reproducibility of SALDI-TOF MS and reduce the

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fragments interference in low mass region. Actually, the particle-size distributions of most currently applied carbon-based matrices (such as CNTs, graphene) were quite wide (from nanometer to micro-, or even larger), which thus resulted in spotting non-uniformity on the LDI target and labile laser desorption/ionization efficiency [37–39]. However, sorting or sizing of

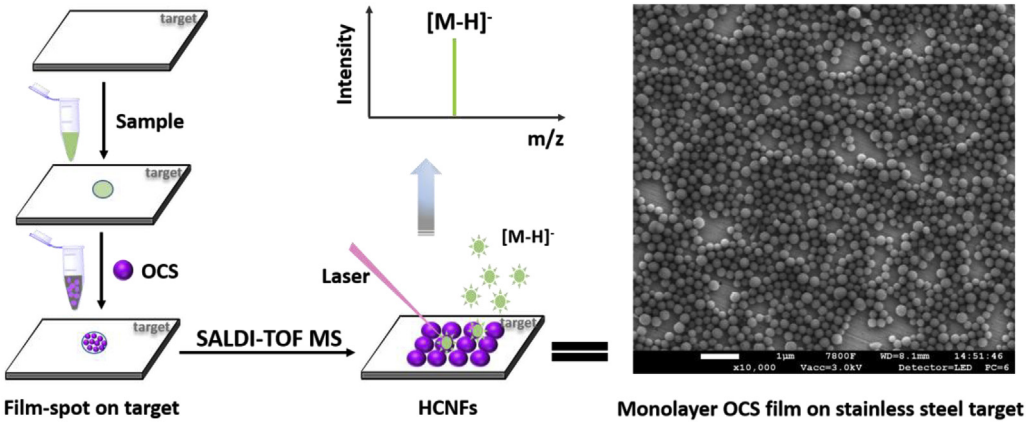

Fig. 1. Diagram represents the formation of homogeneous carbon nanosphere film-spot (HCNFs) on LDI target for laser desorption/ionization of small molecules. (A colour version of this figure can be viewed online.)

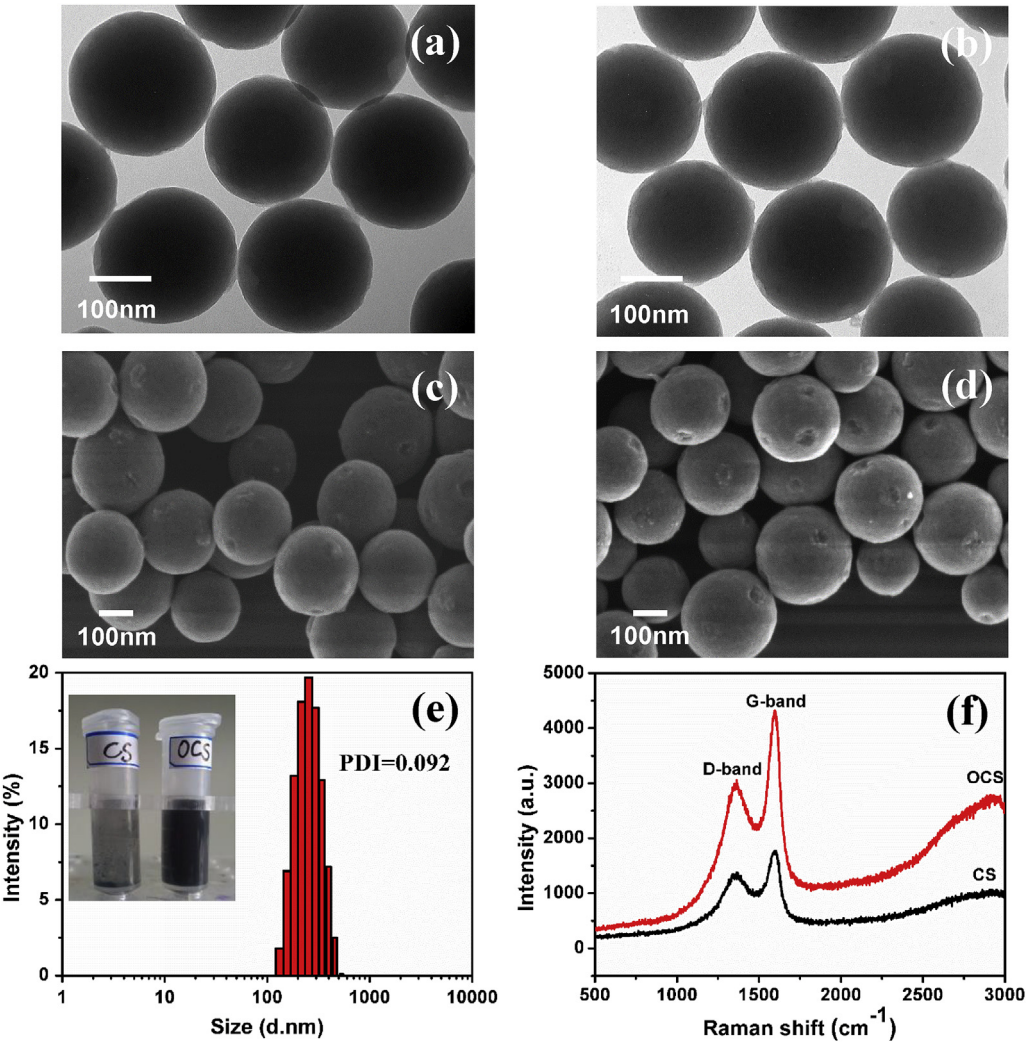

Fig. 2. TEM and SEM images of (a, c) carbon nanospheres (CS) and (b, d) oxidized carbon nanospheres (OCS). (e) Size distribution histograms of OCS measured by dynamic light scattering, the up-left inset was the photos of CS and OCS aqueous dispersion; (f) Raman spectra of CS (black line) and OCS (red line). (A colour version of this figure can be viewed online.)