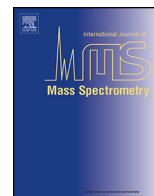




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Impact of analyte ablation and surface acidity of Pd nanoparticles on efficiency of surface-assisted laser desorption/ionization-mass spectrometry

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ABSTRACT

In this study, the impact of analyte ablation and substrate surface acidity on ion yield in surface-assisted laser desorption/ionization-mass spectrometry (SALDI-MS) from Pd nanoparticles was examined. The extent of analyte removal from the Pd material was investigated by X-ray analysis and compared to conventional desorption/ionization on silicon (DIOS) and matrix-assisted laser desorption/ionization (MALDI). Despite the different surface morphologies of the investigated materials and the widely varying ionization yields observed during the experiments, virtually the same amount of analyte was removed by laser irradiation from each of the investigated substrates at a given laser fluence. Our experiments therefore suggested that the extent of analyte ablation from the substrate was less important for SALDI efficiency than the chemical properties of the surface.

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1. Introduction

The number of studies utilizing matrix-free techniques for surface-assisted laser desorption/ionization-mass spectrometry (SALDI-MS) has significantly increased over the past decade [1], because of the soft nature of the ionization process, reduced energetic requirements as compared to matrix-assisted laser desorption/ionization (MALDI), avoidance of “sweet” spot phenomena and the limited background signals in the low m/z range, making SALDI-MS particularly interesting for the analysis of low molecular weight compounds [1].

Numerous functional materials have been implemented for SALDI, including porous silicon (DIOS, desorption/ionization on silicon) [2], porous graphite and graphite nanoparticles (NP) [3], metal nanoparticles and nanostructured coatings [4,5] and many others [1]. Several of these materials have shown promising performance for a wide range of compounds. For example, in a recent study, Sekuła et al. demonstrated that Au nanoparticles (Au-NP) were well suited to the analysis of nucleosides, saccharides, amino acids,

glycosides and nucleic bases as well as over 100 endogenous compounds in imaging mass spectrometry experiments [6]. As well, silver nanoparticles were applied to a wide variety of biological molecules of different structures [7]. On the other hand, numerous SALDI materials have not shown the same universal applicability for diverse chemical structures as seen for established MALDI matrices [8–10] and often work only for specific compound classes.

Differences of analyte response seen for MALDI and SALDI can be rationalized by considering the fundamental difference of the processes involved in the transfer of the proton/cation from substrate/matrix to the analyte molecule. In previous studies, we have explored the impact of surface disorder, thermal conductivity, melting effects, availability of reagent ions, optical properties and surface morphology of Pd-NP during laser irradiation on SALDI response [11–14]. In addition, the contribution of adsorbed water and analyte acidity has been established for porous graphite and silicon substrates as critical parameters, highlighting the important role of the substrate's surface chemistry (e.g., hydrogen bonding, van der Waals interactions) during ion formation [15]. Unfortunately, to our knowledge, no systematic SALDI-MS studies have examined the influence of the surface acidity and the surface desorption ability for metal NPs. We believe that these parameters must be investigated and understood, to allow design of multi-functional materials with universal SALDI behavior, similar to established MALDI matrices.

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This paper investigates two aspects involved in the ion formation during SALDI from metal Pd-NPs: the extent of analyte removal by laser ablation and the surface acidity, and their contribution to SALDI activity. Both aspects were compared to MALDI and DIOS materials.

2. Experimental

2.1. Chemicals and materials

Lactose, glucose, sulfamethazine, reserpine, bradykinin, 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6-ether), α -cyano-4-hydroxycinnamic acid (CHCA), PdCl₂, (NH₄)₂HPO₄, Na₂HPO₄·12H₂O, NH₄Cl, NH₄OH, KOH, and HF (46%) were obtained from Sigma–Aldrich (Steinheim, Germany). Acetonitrile, trifluoroacetic acid (TFA), tetrahydrofuran, methanol, and acetone were from Merck (Darmstadt, Germany), MassPREP DIOS targets were from Waters (Milford, MA, USA), and silicon wafers (boron-doped Si(100), *p*-type, resistivity 0.008–0.012 Ω cm) were from Sumco (Tokyo, Japan); stainless steel alloys (type 309, Fe >50%, Cr 16–26%, Ni 6–22%) with low carbon content (\leq 0.2%) and melting point of 1398–1454 °C were from MHA Zentgraf (Saarbrücken, Germany). Organic-free, de-ionized water was generated by an Elga PureLab (Celle, Germany) water purification system.

2.2. Sample preparation

For analysis of sulfamethazine, carbohydrates and bradykinin, stock solutions at 500 ng/mL were prepared in water (for reserpine, acetonitrile was used). A concentration of 250 ng/mL for 18-crown-6-ether for detection of alkali ions was used. Working solutions were obtained by diluting the stock solutions to the required concentration levels. Analyte solutions (1 μ L) were spotted directly onto the SALDI targets using a pipette and spots were dried under ambient conditions (the spot sizes was depend on the solvent composition). MALDI experiments were performed using the dried droplet method (1 μ L) by mixing equal volumes of analyte and CHCA matrix solution (5 mg/mL in 50:50 [v/v] water/acetonitrile).

2.3. SALDI target preparations

DIOS non-porous silicon wafers were used as is; boron-doped Si(100) wafers were cut into 2.5 cm \times 2.5 cm squares, sonicated in HF for 30 s and washed in acetone and methanol for 10 min. Galvanic Pd-NPs were synthesized on steel as described before [11,12]. To determine the influence of target pH on LDI performance, KOH was additionally used to create basic pH conditions during electrolysis. To describe desorption/ionization efficiencies of SALDI targets, we used the response (sensitivity), $S=I/c$ [19], where I was the analyte's ion current and c the concentration of analyte (ng per spot).

2.4. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

A SEM system from Quanta (Hillsboro, OR, USA) 400 FEG and EDX X-ray spectral analysis system EDAX (Mahwah, NJ, USA) Genesis V 6.04 were used. SEM images were taken in high vacuum mode at 5 kV accelerating voltage (30 μ m final lens aperture size; spot size 3; pixel dwell time 30 μ s, image size 1024 \times 884 pixels). X-ray spectral analysis was performed for 100 s at 5 kV accelerating voltage. X-ray spectra were baseline and ZAF-corrected using the EDAX Genesis software, providing elemental compositions (atomic percent).

2.5. Quantification of the amount of ablated analyte

The amount of ablated analyte after laser treatment for all SALDI substrates and MALDI crystal surfaces was determined by correlative electron dispersive X-ray (EDX) spectroscopy. To obtain a sufficient signal for the analytes during X-ray analysis, the thickest part of the dried analyte was chosen for EDX quantification; the same position on the dried spots was investigated before and after laser treatment. Sulfamethazine was chosen as marker compound using 250 ng per spot, which was an optimal concentration for EDX experiments with reliable counting statistics.

2.6. Transmission electron microscope (TEM)

To investigate internal structures of galvanic targets, the deposits on the steel carrier surface were scratched using sand paper (P600 grit size). A water droplet was placed on the scratched surface to suspend fragments of Pd. A perforated carbon TEM S147-4 grid (Plano, Wetzlar, Germany) was dipped into the suspension and dried on filter paper. TEM measurements were performed using a Jeol (Akishima, Japan) JEM-2100 microscope (LaB₆ cathode, $E=200$ keV) equipped with a Thermo (Waltham, MA, USA) Noran System 7 X-Ray Microanalysis System (EDX). The scratched fragments were investigated by EDX to investigate origin and composition of the Pd deposits. Bright field TEM images were measured using CL1 and HC2 aperture settings. 1024 \times 1024 pixel images were taken using a Gatan Orius SC1000 CCD camera at $t=0.5$ s and binning setting of 2.

2.7. X-ray diffraction (XRD)

For X-ray diffraction measurements, a PANalytical (Almelo, The Netherlands) X'Pert PRO (MRD) system was used. All measurements were carried out under grazing incident conditions ($\Theta=0.6^\circ$, 0.5° fixed divergence slits, 0.04 rad Soller slits, 0.5° anti-scatter slits on the incident beam, 0.27 rad parallel beam optics with a graphite monochromator and a scintillator detector on the diffracted beam) using copper radiation (40 kV, 30 mA) from 20° to 130° 2Θ with a 0.02° step size and 15 s per step. The data were analyzed by TOPAS V4 (Bruker AXS, Karlsruhe, Germany) software. As reference targets, sputtered Pd-films prepared as described before and Pd-foil (99.9%) from Heraeus (Karlsruhe, Germany) were used [11].

2.8. Raman microscopy

Raman experiments were performed on a HORIBA Jobin Yvon (Longmujean, France) LabRAM HR Evolution Raman microscope at ambient conditions using an excitation wavelength of 532 nm (Nd:YAG laser, Melles Griot, IDEX Optics and Photonics, Albuquerque, NM, USA). Raman emission was analyzed using an Olympus (Shinjuku, Japan) 100 \times /0.80 LWD objective and dispersed using 1800 lines/mm grating.

2.9. Reflectivity measurements

Optical characterization of synthesized Pd nanostructures was performed using a Cary 5000 spectrophotometer (Varian, Darmstadt, Germany) in reflectivity mode at 298 K (200–800 nm).

2.10. SALDI and MALDI mass spectrometry

MALDI and SALDI experiments were performed on a Bruker (Bremen, Germany) Esquire HCT+ ion trap mass spectrometer equipped with a MassTech (Burtonsville, MD, USA) atmospheric pressure (AP)-MALDI ion source and Nd:YAG solid-state laser (355 nm, 200 Hz repetition rate, 3 ns pulse duration, laser fluence

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