analytical chemistry

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Electrospun Nanofiber Mats as "Smart Surfaces" for Desorption Electrospray Ionization Mass Spectrometry (DESI MS)-Based Analysis and Imprint Imaging

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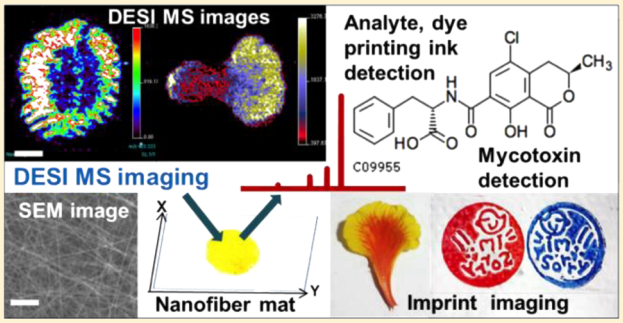
Supporting Information

ABSTRACT: In this paper, desorption electrospray ionization mass spectrometry (DESI MS)-based molecular analysis and imprint imaging using electrospun nylon-6 nanofiber mats are demonstrated for various analytical contexts. Uniform mats of varying thicknesses composed of ~200 nm diameter fibers were prepared using needleless electrospinning. Analytical applications requiring rapid understanding of the analytes in single drops, dyes, inks, and/or plant extracts incorporated directly into the nanofibers are discussed with illustrations. The possibility to imprint patterns made of printing inks, plant parts (such as petals, leaves, and slices of rhizomes), and fungal growth on fruits with their faithful reproductions on the nanofiber mats is illustrated with suitable examples. Metabolites were identified by tandem mass spectrometry data available in the literature and in databases. The results highlight the significance of electrospun nanofiber mats as smart surfaces to capture diverse classes of compounds for rapid detection or to imprint imaging under ambient conditions. Large surface area, appropriate chemical functionalities exposed, and easiness of desorption due to weaker interactions of the analyte species are the specific advantages of nanofibers for this application.



Ambient ionization mass spectrometry, in particular, desorption electrospray ionization mass spectrometry (DESI MS), has received widespread attention in the analysis of molecules at surfaces.[1] Innovations in instrumentation and advances in the family of ambient ionization methods illustrate the capabilities currently available.[2] Using such techniques, direct detection of the compounds of interest without extraction and sample pretreatment are being explored for several complex samples.[3] Over the years, although diverse ionization techniques have gained importance, the need for versatile substrates for surface analysis has not been addressed. DESI MS imaging, in particular, requires flat, rigid surfaces to tolerate high pressure of the nebulizing gas, and the continuous flow of solvent during the desorption process. Capturing molecular signatures, faithfully registering them, and revealing them without losing spatial information for a diverse variety of chemical species are important attributes of a reliable and versatile substrate used in DESI MS. Thin layer chromatography (TLC) plates have been the most successful for many analytical systems including imaging mass spectrometry. Surfaces reported for ambient ionization mass spectrometry include polytetrafluoroethylene (PTFE), TLC-plates, porous silicon, and nanoporous alumina, etc.;[4−7] nevertheless, these surfaces have some limitations; PTFE has no porosity and is hydrophobic, whereas oxide supported in TLC plates could contribute to catalytic as well as photochemical degradation of materials imprinted on them. Long-term storage of such imprints could lead to reactions stimulated by light or ambient conditions. These limitations prompted us to explore new surfaces/substrates with improved capabilities.

Nanofibers (of diameter in the regime 50 nm to several micrometers) are fibrous matrices prepared from a combination of both inorganic and organic substances. Electrospinning, a versatile technique for the fabrication of nanofibers, is often used to tailor the morphologies, surface chemistries, special properties, and functions.[8,9] The availability of large surface area, porosity, and increased sites for analytes' interactions lead to the success of electrospun nanofibers in analytical processes.[10] Besides serving as superior chromatographic stationary phases for low and high resolution separation,[11] nanofibers are used in tissue engineering, drug delivery, water purification, and solar cells, as chemical and biological sensors, etc.[12,13] To cater to the needs of such heterogeneous applications, nanofibers are made from a wide range of combinations of polymers with added functionalities and/or morphological modifications.[14,15] Characterization of nanofibers is done routinely using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), thermogravi-

Received: November 29, 2015
Accepted: May 9, 2016
Published: May 9, 2016

DOI: 10.1021/acs.analchem.5b04520
Anal. Chem. 2016, 88, 5710−5717

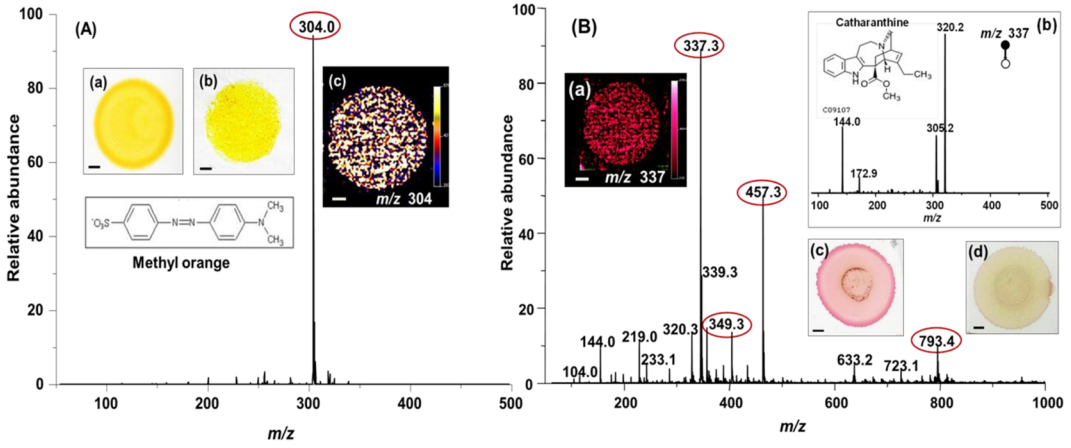


Figure 1. (A) DESI MS spectrum eluted from a spot sample of methyl orange on a nylon nanofiber mat. (a) Photograph of the corresponding spot on a TLC-plate showing the spreading effect, forming a halo on the periphery. (b) Same sample spotted on a nylon nanofiber mat showing uniform spreading. (c) DESI MS image of a methyl orange peak at m/z 304. (B) DESI MS spectrum of a Madagascar periwinkle flower extract spotted on an electrospun nylon nanofiber mat. DESI MS image (a) and tandem mass spectrum (b) of Catharanthine at m/z 337. TLC-plates showing the spreading (c) and fading effects (d) of the spot of the flower extract. The scale bar in all DESI MS images is 5 mm.

metric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), etc.[16] We propose that the inherent properties and versatility of the nanofibers may be used for direct sampling of molecules.

Mass spectrometry (MS) based methods are rarely used to study nanofibers, despite being made of synthetic or natural polymers or polymer blends. MS has been used on a variety of polymers to understand their surface chemistry, structural properties, interactions, and/or even degradation products.[17,18] As a vast majority of synthetic polymers are relatively nonpolar, and do not ionize easily, they are not suitable for ionization based on polar solvents, such as electrospray ionization.[19] Fine tuning of instrumental parameters is suggested to achieve ionization of polymers or even to suppress noise/signals from polymeric surfaces in ambient ionization methods.[20]

This study demonstrates the use of electrospun nanofiber mats made of nylon-6 (a widely used polymer for both biomedicine and other applications)[21,22] as smart surfaces for rapid detection or imaging by DESI MS under ambient conditions. The feasibility of using methanol as a spray solvent on nylon nanofiber mats to detect/image analytes/metabolites without the interference of the polymeric substrate is illustrated for six different bio/analytical contexts. We believe that the flexibility in making different substrates, the surface functionalization of the fibers, and the enhanced properties of the nanofiber mats will expand the scope of ambient ionization mass spectrometry.

EXPERIMENTAL SECTION

Materials. Polyamide-6 (Nylon-6, M_n = 10 000 g/mol), formic acid, methanol, and acetonitrile were purchased from Sigma-Aldrich. Marker pens and printing inks, used for imaging, were of Faber-Castell brand, purchased from a local store. Plant parts, such as petals of Madagascar periwinkle (*Catharanthus roseus* (L.) G. Don), Poinciana (*Caesalpinia pulcherrima* (L.) Sw.), leaf of betel (*Piper betel*, L.), and rhizome of turmeric (*Curcuma longa*, L), were collected from the nursery of IIT Madras, Chennai campus, or the local market of Chennai.

Electrospinning of Nanofiber. An electrospinning setup—Nanospider NS 200S[23] from Elmarco—was used for preparing nanofibers (video S1). Nylon-6 was dissolved in formic acid at 60−70 °C and stirred for at least 18 h prior to use. The solution in formic acid was prepared in three concentrations: 18, 16, and 12% (w/w). These concentrations were optimized for the reproducible production of smooth and uniform fiber morphologies (Figure S1). Tetraphenylphosphonium bromide (TPPB, 5 mg) and periwinkle flower petals (5 mg) were dissolved/extracted in 1 mL of methanol, and the solution was added to nylon-6 solution. The mixture was stirred for 1 h at room temperature prior to electrospinning, and it was then electrospun at room temperature. The polymer solution was placed in a cylinder containing the active electrode parallel to the collecting electrode. The polymer solution was delivered at a distance 18 cm from the active electrode to the collecting electrode by applying a voltage of 70 kV, with the electrode rotating at a speed at 2.3 rpm, at relative humidity of 35−45%. The fibers were collected on an aluminum sheet. An as-prepared electrospun mat was dried inside the hood at room temperature for an hour. A portion of the mat was used for characterization purposes, and the rest of the nanofiber sample was dried in a moderate vacuum (∼50 Torr) overnight and stored in zip lock polybags until use. The morphology of the as-prepared electrospun mat was studied using scanning electron microscopy (SEM) (FEI QUANTA-200) as per the standard protocols.[24]

Mass Spectrometry Imaging. For mass spectrometry imaging, a Thermo Finnigan LTQ linear ion trap mass spectrometer equipped with a DESI source (Prosolia Inc., CA) was used. To avoid damage to the nanofiber surface, the nanofiber mat along with the aluminum foil was cut in the desired dimension and fastened onto the glass plate of the DESI stage using double sided tape. Imprinting of a plant leaf and a flower petal on the nylon mat was done as described previously.[25] For making patterns with printing inks, stamps with definite patterns were coated with a printing ink and imprinted manually on the nanofiber mat. The spray solvent for MS acquisition in the positive and negative ion modes was methanol or methanol:water (50:50) or acetonitrile, and a spray voltage of 4.5 kV was applied. The nitrogen gas pressure was 100 psi, and the solvent flow rate was 3 μL/min. In imaging experiments, the imprinted nanofiber was scanned using a 2D moving stage in horizontal rows separated by a 250 μm vertical

DOI: 10.1021/acs.analchem.5b04520
Anal. Chem. 2016, 88, 5710−5717

step until the entire sample was imaged. All experimental data were acquired using a LTQ linear ion trap mass spectrometer controlled by XCalibur 2.0 software (Thermo Fisher Scientific, San Jose, CA). The Firefly program allowed the conversion of the XCalibur 2.0 raw files into a format compatible with the BioMap (freeware, http://www.maldi-msi.org) software. The individual spectra or pixels that were acquired were assembled into a spatially accurate image using the BioMap software.

RESULTS AND DISCUSSION

The versatility of electrospun nylon nanofiber mats for multiple applications is illustrated in Figures 1−6 and Figures S3 and S4. Materials most commonly available for these applications are TLC plates and printing papers; hence, they are compared with nanofiber mats. The same instrumental parameters, spray solvents as optimized/reported for TLC plates, and printing paper were applied for nanofiber mats to illustrate their superiority in all the experiments. Nanofibers are tunable to achieve the desired properties by varying spinning conditions/surface functionalization, the advantage of which is available in numerous reports;[12−16] hence, we restricted the discussion to the context of our results. Nanofiber mats of desired thicknesses were prepared by needleless electrospinning using Nanospider as shown in video S1. SEM images (Figure S1(a−f)) show the morphologies and thickness of the fiber mats produced. The fiber mats appear as thin polymer films, white in color (Insets (i−iii) of Figure S1(a−c)). Fiber mats formed on aluminum sheets were cut into the desired shapes as necessary. The fibers were 200−1000 nm diameter. The thicknesses of the nanofiber mats used for surface analysis were 50−100 μm (Figure S1(d,e)) and 150−170 μm (Figure S1(f)), and those mats were subsequently used for imprinting.

For Detection/Imaging of Analytes in a Single Drop. Figure 1A,B illustrates the use of a nylon nanofiber mat for direct measurement of analytes in a single drop. Analytes may be colored or colorless ones. Trace detection of analytes has been demonstrated using DESI MS for a number of analytes.[26] When a single drop of methyl orange (MO) (colored) dye or periwinkle flower extract (colorless) was spotted on the TLC plate, the contents of the analytes were spread and became concentrated at the periphery, forming a halo, as shown in Figures 1A(a) and 1B(c). Spotting analytes on a nylon nanofiber mat gave a uniform coating without a halo (Figure 1A(b)), enabling a reproducible DESI MS image (Figure 1A(c)). Images were detectable in both positive and negative ion modes; the characteristic peak at m/z 304 for MO was in negative ion mode (Figure 1A) whereas the alkaloid peaks of periwinkle flower extract were detected in positive ion mode (Figure 1B). Peaks at m/z 337, 457, and 349 (encircled in Figure 1B) were confirmed by tandem mass spectral data (Figure 1B(b)) as catharanthine, vindoline, and serpentine, respectively, which matched exactly with our previous report.[25] The flower extract spot on the TLC-plate (Figure 1B(c)) became discolored within 10 days during storage under ambient conditions (Figure 1B(d)). For the MO spot on a TLC-plate, similar fading of the imprinted dye color (for both the peripheral halo (Figure S2(a)) and the interior (Figure S2(b) regions) was noticed in 2 weeks; tentative assignment of peaks (Figure S2) using the literature[27] showed the degradation products of MO. Besides being suitable for imaging analytes, nylon nanofibers act as effective sorbent materials[22] and could be better substrates to study dyes and other contaminants in water.

For Imaging of Incorporated Materials/Agents. Compounds of interest can be incorporated into nanofibers during formation, which becomes an advantage over other surfaces. It is crucial to understand the pre and post modifications for any imaging agents/drugs (biological or chemical) that are selectively incorporated or immobilized into polymeric materials.[28] To study the fate of such incorporated materials, nylon nanofibers was incorporated with (1) crude methanol extract of periwinkle flower (Figure 2) or (2) an imaging agent,

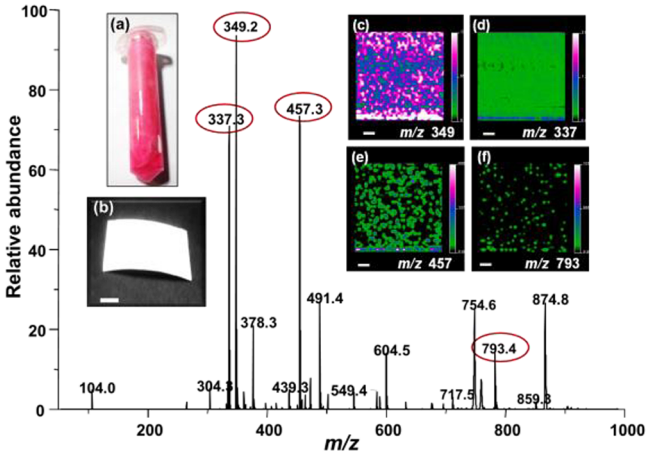


Figure 2. DESI MS spectrum of a periwinkle flower extract incorporated electrospun nylon fiber mat. (a) Polymer blend with flower extract showing a pink colored solution. (b) Optical image of the flower extract-incorporated nanofiber mat after electrospinning. (c−f) DESI MS images of the encircled peaks at m/z 337, 349, 457, and 793. A uniform distribution of the compounds is seen. The scale bar in all DESI MS images is 5 mm.

tetraphenylphosphonium bromide (TPPB)[29] (Figure S3) and imaged with DESI MS. When the periwinkle flower extract was blended with the nylon polymer solution, it became pink in color (Figure 2C (a)), but the resultant nylon mat was white after electrospinning. Major metabolites peaks of periwinkle (encircled in Figure 2) could be identified by MS^n imaging. Tandem mass spectrum confirmed the incorporated metabolites, though the concentration of each metabolite in extract was unknown. Spectral similarities/differences between Figure 1B and Figure 2 show the changes due to spotting and incorporation of flower extract. Low concentration of TPPB (~100 ppm) also gave an intense peak at m/z 339 (Figure S3), characteristic of TPPB without any interference from the nylon. Tandem mass spectrum (Figure S3 (b)) was used to confirm the incorporation of TPPB. The above results demonstrate the compatibility of nylon polymer with the extract and imaging agent. The suitability for desorption/ionization process, negligible background and noninterference nature[30] establishes electrospun nanofibers as smart surfaces for mass spectrometry. Thus, the use of nanofiber mats in conjunction with DESI MS may be a rapid method to study the compatibility of polymers, their interactions and fate of the incorporated (bio/chemical) agents over time.

For Detection/Imaging the Effect of Spray Solvents/Wetting on Nanofiber Mat. The choice of solvent is crucial for desorption of analyte molecules from the surface, transfer into the gas phase, and subsequent ionization. The solubility of the analytes, the interaction of solvent with the surface, and the nature of secondary droplets leaving from the surface would

DOI: 10.1021/acs.analchem.5b04520
Anal. Chem. 2016, 88, 5710−5717

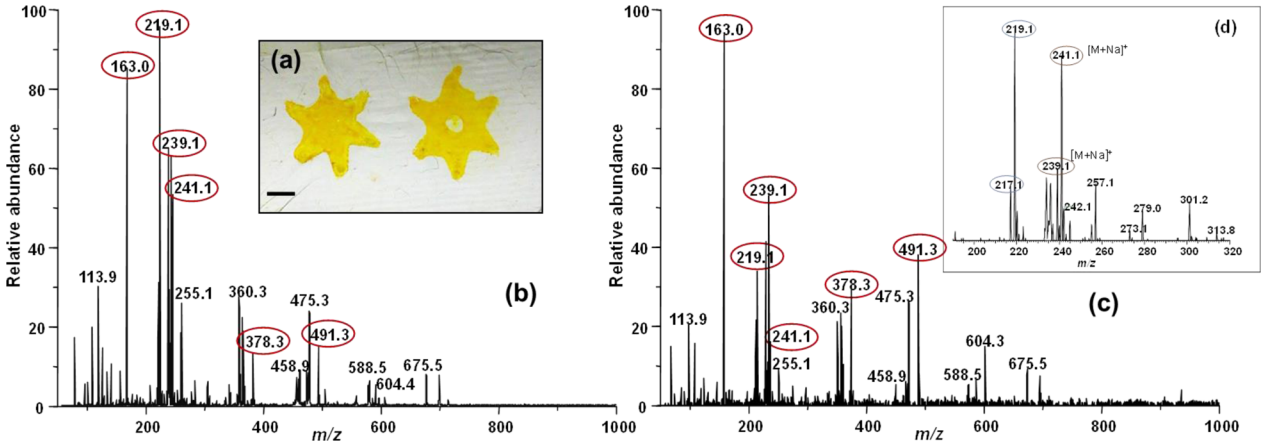


Figure 3. (a) DESI MS spectrum from a turmeric extract imprinted pattern on a nylon nanofiber mat. (b,c). Spectra showing that the intensities of the encircled peaks became changed during wetting. (d) Peaks encircled in blue and red are sodium adduct peaks of α-turmerone and curlone. The scale bar in (a) is 5 mm.

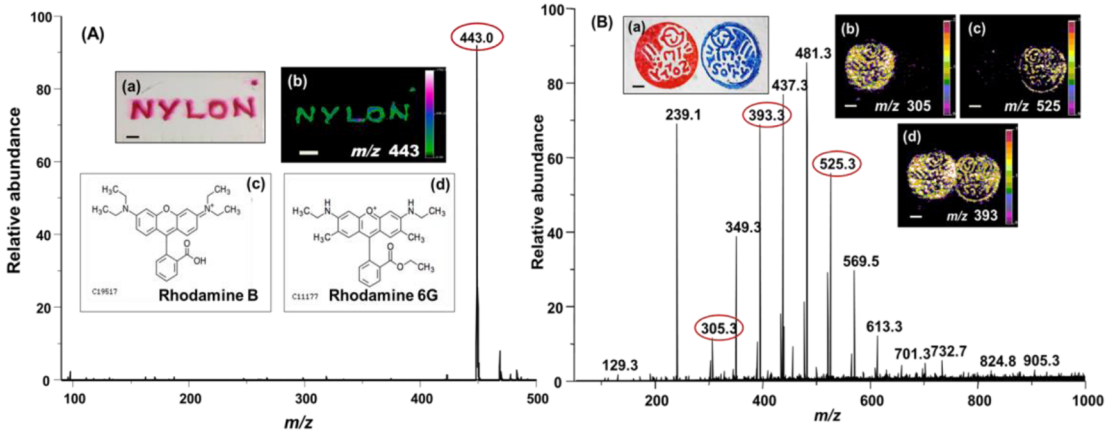


Figure 4. (A) DESI MS spectrum showing the peak at m/z 443 collected from an image made with a red marker pen, a photograph of which is shown in (a). Inset (b) is the DESI MS image of the mat with a red colored text "NYLON" recorded using m/z 443, which may be (c) Rhodamine B or (d) Rhodamine 6G. (B) DESI MS spectrum showing peaks from pictorial patterns made of red and blue colored printing inks imprinted close to each other on a nylon nanofiber mat, as shown in optical image (a). (b–d). DESI MS images corresponding to the imprinted patterns. The scale is uniform in all the images (5 mm).

influence DESI efficiency.[31] A stamp pattern coated with turmeric extract was imprinted on a nylon nanofiber mat (Figure 3 and Figure S4) to demonstrate the effect of spray solvents and wetting.

Turmeric extract has been used as a dye and a therapeutic agent.[32,33] Curcumin (diferuloylmethane), an orange-yellow bioactive component of turmeric, is loaded in nanofibers for biomedical applications.[33] As curcumin is insoluble in water, turmeric extract, having solubility and better biological effects than purified compounds,[34] is preferred for use. Hence, we used methanol extract of fresh turmeric rhizome as a dye to imprint a pattern as shown in Figure 3(a) on a nylon nanofiber mat; the imprinted mat was dipped in water, dried, and then imaged. Though the patterns on the nylon nanofiber mat seemed to be intact to the naked eye, subtle distortions showing release of some molecules were observed in DESI MS images (Figure S4A(b–e)). Peaks encircled with red in Figure 3 and Figure S4A show the variations in peak intensities induced by wetting which lasted for 30 s (Figure 3(b)) and 5 min (Figure 3(c), Figure S4A). Details on the protonated mass spectra and fragmentation pattern of curcuminoids and other phytochemicals in turmeric extract[35] were used in understanding the changes observed. Evaluation of changes at the surface during wetting/solvent spray would help in understanding the interaction/noninterfering nature of the substrate. Also, interlaboratory variations are possible due to adduct(s) and other contaminations.[36] The possibility to compare the intensity of adduct formation while using solvents on nanofiber substrates is illustrated in Figures 3 and Figure S4B. Encircled peaks at m/z 239 and 241 in Figure 3(d) show the intensity of the sodium adduct peaks of α-turmerone and curlone,[35] when methanol was used as the spray solvent. Comparison of the spectrum of Figure 3 with that of Figure S4B(a) (methanol:-water) and Figure S4B(b) (acetonitrile) showed that the intensities of the adduct peaks were low for acetonitrile. Figure S4C illustrates the effect of spray (methanol:water) solvent on a similar pictorial pattern made of turmeric extract on printing paper (Figure S4C(a)). The disturbance created by the spray solvent (methanol:water) on the pictorial pattern resulted in a distorted DESI MS image (Figure S4C(b) though the spectrum was similar to that of Figure S4C(a)). Thus, based on analytical needs, nylon nanofiber substrates allow the selection of suitable solvents to obtain a cleaner mass spectrum. An added advantage of nanofiber mats is that the surface charge on the

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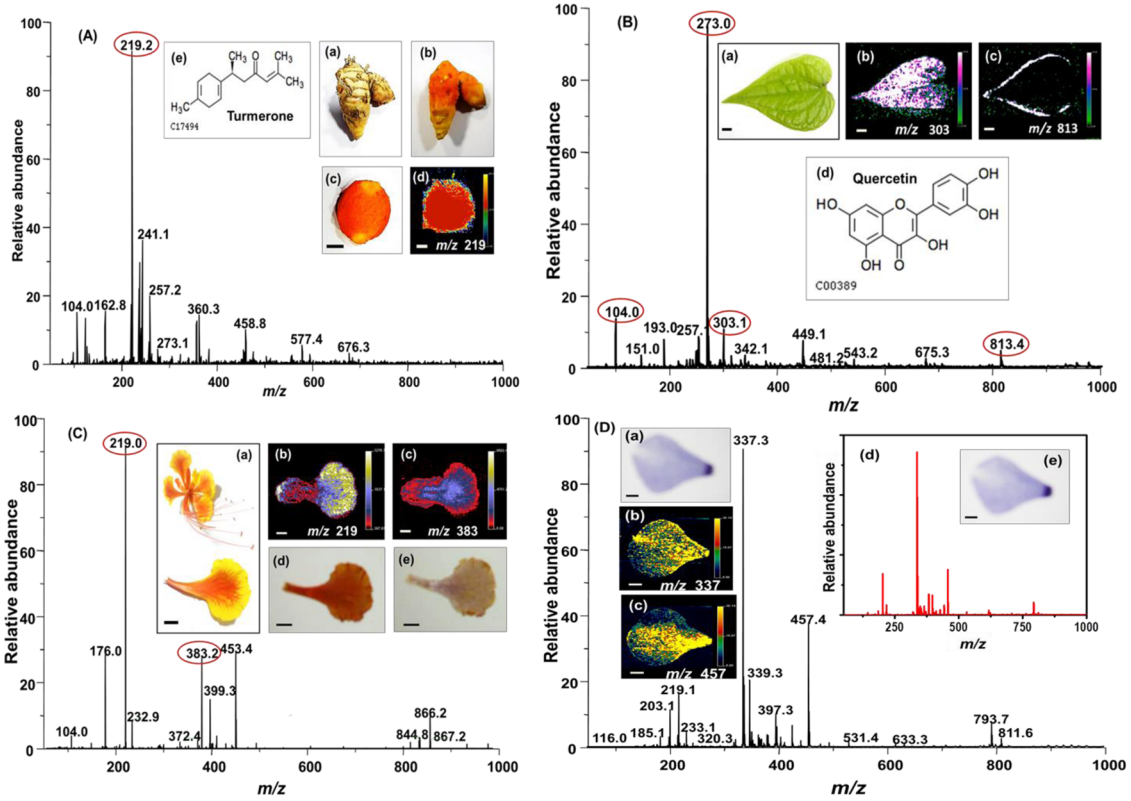

Figure 5. (A) DESI MS spectrum from a turmeric rhizome slice of an imprinted nylon nanofiber mat. (a,b) Optical images of a whole and unskinned turmeric rhizome. (c) Imprinted slice on a nylon nanofiber mat. (d) DESI MS image at m/z 219 due to α-turmerone shown in (e). (B) DESI MS spectrum of betel leaf (a) photograph and (b,c) DSEI MS images of imprinted patterns on nylon nanofiber mat. (d) Structure of the molecule attributed to m/z 303. (C) DESI MS spectrum of poinciana flower petal, (a) imprinted nanofiber and the corresponding DESI MS images (b,c). Corresponding imprint on TLC plate (d) and its fading effect (e) upon storage. (D) DESI MS spectrum of Madagascar periwinkle petal imprinted nylon nanofiber mat (a) and corresponding reproducible spectrum (d) from the imprint (e) after 2 weeks of storage. (b, c) DESI MS image of metabolite ions corresponding to catharanthine at m/z 337 and vindoline at m/z 457. Scale in all images is 5 mm.

mat could be tailored as positive or negative by altering the applied voltages during spinning.[37] Also, by tuning the critical thickness and porosity of the nanofiber mats, the penetration/wetting of water/solvents could be tailored, besides dissipating the effects of surface tension and viscosity.[38]

For Imaging Imprinted Patterns of Inks. Spectral contamination from the underlying substrate is the major difficulty in forensic analysis of inks, even with nondestructive methods including DESI MS.[39] Here, we have illustrated the utility of an electrospun nylon nanofiber mat in eliminating spectral contamination in such cases. Figure 4A shows that a hand-written word made of red marker pen on the nylon nanofiber mat was faithfully reproducible in DESI MS images. The signal observed at m/z 443 may be due to cationic dye Rhodamine 6G or Rhodamine B which could be confirmed with the photodegradation products available in the literature and databases.[39] When two or more marker pens were used on a printer paper, the carryover effect of one over the other may happen as in Figure S5A. The disturbance created by spray solvent on the DESI MS image using imprinted paper is shown in Figure S5B. Though DESI removed low (attomole) amounts of ink,[40] instrumental parameters such as the solvent flow rate, distance of the spray from the sample, line scan speed, spacing, and time have to be optimized for reducing such carryover effects.[41] The advantage of the nylon nanofiber mat is that even pictorial patterns made of printing inks could be imaged, however close they may be. Figure 4B(a) shows picture stamp patterns made of red and blue colored printing inks imprinted very close to each other on the same nylon nanofiber mat. The corresponding DESI MS images show the reproducibility, and there were no overlaps or spectral contamination; besides, there was a possibility to detect an image from color(s) either individually (Figure 4B(c,d) or together (Figure 4B(b)). A searchable reference library is available for most of the commonly used inks. As printing inks composed of complex mixtures of organic and inorganic components could be discriminated based on mass spectral data,[42] our results demonstrate that nylon nanofiber mats are suitable surfaces in the analysis of inks.

For Imaging Imprinted Plant Parts. The amenability of nylon nanofiber mats for the imprint imaging of plant parts (petal, leaf, and rhizome) is illustrated in Figure 5. As a flat, stiff surface was needed for making imprints, thick mats of size 150−170 μm (Figure S1(f)) prepared with 18% nylon, were used. To facilitate imprinting on nylon mats, methods reported from our research group and in literature were followed.[21,25] A cut slice of fresh turmeric rhizome imprinted manually on a nylon nanofiber mat (Figure 5A) was used to record DESI MS images. Tandem mass spectrometry was done on high intensity peaks in both the ion modes. Here, the intense protonated ion at m/z 219 corresponds to α-turmerone (Figure 5A(e)): an aromatic compound responsible for the aroma of the turmeric rhizome. Likewise, metabolite ions for the classes of compounds (curcuminoids, diarylheptanoids, sesquiterpenes, phenolics, and other flavonoids) were assigned using a database search and with available reports in the literature.[35] Metabolites

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identified in negative ion mode include a few curcuminoids (demethoxycurcumin (m/z 239), bisdemethoxycurcumin (m/z 309), and curcumin (m/z 369)) and sesquiterpenoids (curcumenone (m/z 335)). Details on the structure, mass, and database reference for some of these metabolites are given in Table S1. Nylon nanofiber imprints retained the aroma of turmeric rhizome besides the natural color and shape; this observation was verified especially with samples such as leaf of betel and petal of poinciana flower (Figures 5B,C). For betel leaf, we show only a few metabolites which are detectable in imprints (Figure 5B), as compared to the ESI MS of the extracts. The major metabolites of betel leaf identified in this study, in both ion modes using their characteristic fragmentation patterns,[43] include charvicol (m/z 135), hydroxycharvicol (m/z 151), eugenol (m/z 165), coniferaldehyde (m/z 179), methoxy eugenol (m/z 195), eugenyl acetate (m/z 207), quercetin (m/z 303), and chlorogenic acid (m/z 355). Though the intensity of the peak at m/z 303 was low, the DESI MS image (Figure 5B(c)) shows high contrast; the feature was identified as due to quercetin (Figure 5B(d) by tandem mass spectrometry. Metabolites contributing to the nectar (namely glucose, fructose, and sucrose) were captured in the nylon nanofiber imprint of a poinciana flower petal (Figure 5C(a)), in addition to the color (flavonoids and anthocyanins).[44] The peaks m/z 203 and m/z 219 were reported as sodium and potassium adducts of hexose, whereas the peaks at m/z 365 and m/z 381[45] (encircled in Figure 5C) were the sodium and potassium adducts of glucose whose spatial distribution is given in Figure 5C(b,c). The degradation of color of a TLC imprinted petal during storage is shown in Figure 5C(e). The periwinkle petal imprints made onto the nylon nanofiber mats may be faint (Figure 5D(a), but DESI images of molecular ions with high contrast could be obtained (Figure 5D(b,c)). The petal color on the nanofiber imprint (Figure 5D(e) lasted for 5 weeks without fading besides giving a reproducible spectrum (Figure 5D(d)). The spectrum of nanofiber imprinted periwinkle petal (Figure 5D) was similar to that of the TLC-imprinted one (Figure S6A), but showed enhancement in the peak intensity of m/z 203 and 219. The TLC-imprint of periwinkle petal was discolored during storage (Figure S6B(a)). There was a concomitant reduction in the ion intensity of the metabolite peaks (m/z 337 and 457) besides the poor DESI image (Figure S6B(b,c)). The enhanced detection of aroma, nectar, and coloring compounds by the nylon nanofiber surface might be due to the availability of a high surface to volume ratio, high porosity, and fibrous surface of the nanofiber.[46]

For Imaging Fungal Growth/Contamination of Fruits. Fungal species growing on food and/or fruits can be rapidly identified using nylon nanofiber mats (Figure 6). The fungal infection on lemon fruit was swabbed with nylon nanofiber mats and imaged. DESI MS images showed the reproducibility of the infection zones along with the details of the metabolites released due to the fungal growth as well as the degradation of lemon fruit. Tandem mass spectral fragments of highly intense peaks showed that the metabolites were both from fungi and the degrading lemon. The major metabolite identified (Figure 6) was at m/z 404, the tandem mass spectra of which confirmed it as Ochratoxin A (OTA). It is a toxic metabolite released by the fungus *Penicillium digitatum*, the causal agent of fruit rot of lemon.[47] Several metabolites, including limonene (m/z 137) and limonene-diol (m/z 171), released by the degrading lemon tissue could also be identified (Table S1, Supporting Information). Direct imaging of microbes from agar

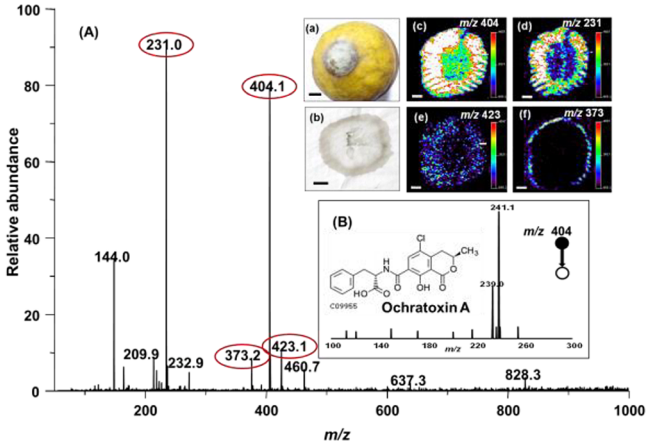

Figure 6. (A) DESI MS spectrum from the fungal infected region of lemon fruit imprinted on a nylon nanofiber mat. (a,b) Optical images of infected whole fruit of lemon (a) from which the fungal infection was swab-imprinted on a nylon nanofiber mat (b). (c–f) DESI MS images of encircled peaks showing toxic fungal metabolites. (B) Diagnostic fragmentation pattern and structure of Ochratoxin A at m/z 404.

plates was reported,[48] but using nanofiber mat eliminates background interference and restrains the microbial contamination.[49]

Several analytes used in this study were complex mixtures (printing inks and plant extracts), wherein the concentration of individual component may vary. Sufficient analyte concentration is required to distinguish analytical signal from noise and limit of blank, while estimating the limit of detection (LOD).[50] Hence, we did not estimate LOD for each analyte. The best resolution possible and the LOD of the nanofiber mat are not discussed in this paper because there are many associated factors which have to be addressed individually. Given below are a few of these issues: (1) With an increase in the thickness of the nanofibers, the cross-sectional structure of the mat would influence the retention of solvents and analyte, desorption, detection, etc., thereby affecting the LOD. (2) With a change in the molecular weight and synthesis process of the same polymer, there will be a change in diameter, porosity, and surface characteristics of the resultant mat;[51] hence, the LOD and the best resolution possible[52] may vary even if measured with the same instrument. (3) Nanofibers are interactive surfaces, and their properties (size, orientation, morphology, polarity, and surface charge states)[12−16,37,38] are tunable through spinning conditions and/or by adding cosolvents (such as acetic acid, dimethyl sulfoxide (DMSO), etc.) or ionic salts during electrospinning. Such surface functionalization of nanofibers with nanomaterials, cosolvents, and other chemicals could enhance or deter the signal intensities irrespective of the instrument performance.

Usually the LOD possible with nylon nanofibers is expressed at a single fiber level. In one of our research papers,[53] LOD for metal ions down to tens of ions was demonstrated with nylon nanofibers; however, that was based on fluorescence. In general, the examples given in this manuscript refer to the suitability of nanofiber mats as substrates for large scale analysis of clinical, biological, or imprinting needs of samples by DESI MS, wherein LOD is not a crucial parameter.

DOI: 10.1021/acs.analchem.5b04520
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CONCLUSIONS

The suitability of nylon nanofiber mats as smart surfaces for DESI MS is illustrated using specific examples, including patterns formed by single drops with dissolved dyes, marker pen inks, and printing inks. No overlapped images were produced from imprinted patterns on nanofiber mats made of inks, however close they may be. The fate of imprinted patterns on wetting was examined with illustrations. Imprints of plant parts (leaf, flower petal, and rhizome) demonstrated the significance of using nanofiber mats as smart surfaces for identifying and preserving diverse classes of compounds, including aroma and color. It was possible to image the fungal species growing on fruit. The results of this study suggest that electrospun nanofiber mats may serve as smart surfaces for rapid detection of molecules or for imprint imaging protocols using DESI MS. As electrospun nanofibers can be made industrially, their use in DESI MS can become a promising method of analysis due to the various advantages presented here.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b04520.

SEM images of electrospun nanofibers; DESI MS spectrum and images showing degradation of the methyl orange spot on the TLC plate; DESI MS image for a tetraphenylphosphonium bromide incorporated nylon nanofiber mat; effect of spray solvents on a turmeric extract imprinted nylon nanofiber mat; DESI MS spectrum and images of marker pen ink patterns on paper; DESI MS spectra and images of a TLC imprint of a periwinkle petal upon storage; identification of metabolites of using a database search (PDF)

Preparation of a nanofiber mat by needleless electrospinning as observed using the instrument Nanospider (NS LAB 200) (AVI)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Department of Science and Technology, Government of India, for equipment support through the Nano Mission. R.G.H acknowledges the Department of Biotechnology, Government of India, for providing a BioCARe woman scientist fellowship.

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DOI: 10.1021/acs.analchem.5b04520
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