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Synthesis of Highly Water-Dispersible Polydopamine-Modified Multiwalled Carbon Nanotubes for Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry Analysis

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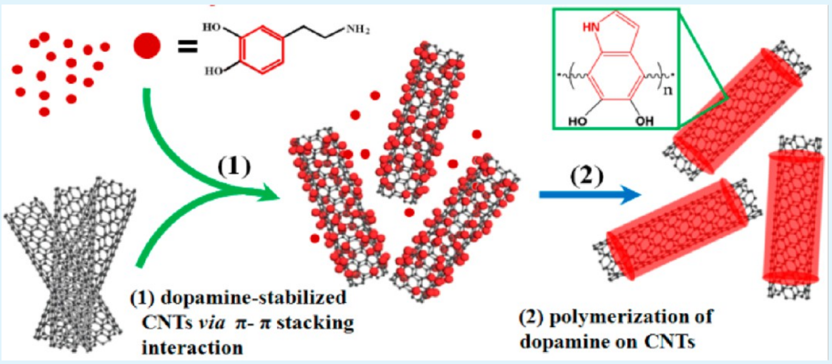
Supporting Information



ABSTRACT: In this work, we synthesized highly water-dispersible multiwalled carbon nanotubes@polydopamine (MWCNTs@PDA) core−shell composites by a facile in situ oxidative polymerization. The composites were successfully applied as a novel matrix for the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF−MS) analysis of various water-soluble small molecule compounds. It was found that MWCNTs@PDA composites have a higher sensitivity and peak intensities for small molecules detection.

KEYWORDS: *MALDI-TOF−MS, matrix, MWCNTs@PDA, small molecules, oxidative polymerization, surface modification*

Matrix-assisted laser desorption/ionization (MALDI), a soft ionization tool developed by Tanaka et al.[1] and Karas et al.[2] in the late 1980s, has become an indispensable analytical approach for use in biochemical analyses and proteomics research. When performed together with the application of a TOF−TOF mass analyzer,[3−5] it also supplies structural information for molecules with a high speed, sensitivity, and accuracy.[6] The tremendous advantages of the MALDI technique are simplified sample pretreatment steps, high salt and buffer tolerance, and high throughput. However, the use of conventional organic matrices, such as α-cyano-4-hydroxycinnamic acid (α-CHCA) and 2,5-dihydroxybenzonic acid (2,5-DHB), has significant limitations for the analysis of small molecules because these matrices break up under laser irradiation and produce undesired interference peaks in the low-weight region (<500 Da).[7] In recent years, much work utilizing trial and error has been made to develop an appropriate matrix composition for successful analysis.[8] Many stable inorganic materials, including porous silicon surfaces and graphitic carbon nanomaterials,[9−13] have been demonstrated as alternative matrices and employed to eliminate interference on the basis of their ability to transfer energy from the laser irradiation to the analytes for the ionization of analytes.

Among the family of carbon nanomaterials, carbon nanotubes (CNTs) with single or multiwalls have stimulated intense interest since their initial discovery by Iijima[14−16] and have become one of the most exciting research topics because of their outstanding properties. Very recently, multiwalled carbon nanotubes (MWCNTs) were introduced as an effective matrix in MALDI-TOF−MS that can avoid matrix ion interference in the low-weight region.[17,18] MWCNTs, composed of π-conjugated networks, have a large surface area, high conductivity, excellent thermal stability, and easy functionalization for manipulating their surface properties.[7,15,16,19−21]In addition, it has been proven that MWCNTs can offer a high laser desorption/ionization efficiency to analytes by absorbing UV laser energy and transferring it to the analytes. Meanwhile, MWCNTs can also simplify sample pretreatment and eliminate the matrix interference peaks in MALDI analysis.[22]

For a reproducible and effective analysis, the MWCNTs matrix should be dispersible in the sample solution so that the every MWCNT is in good combination with analytes, just like a conventional organic matrix (e.g., α-CHCA), which is soluble in solution of analytes. Unfortunately, pristine MWCNTs are highly hydrophobic and cannot be directly dispersed in either aqueous or nonaqueous solutions. To solve this problem, much

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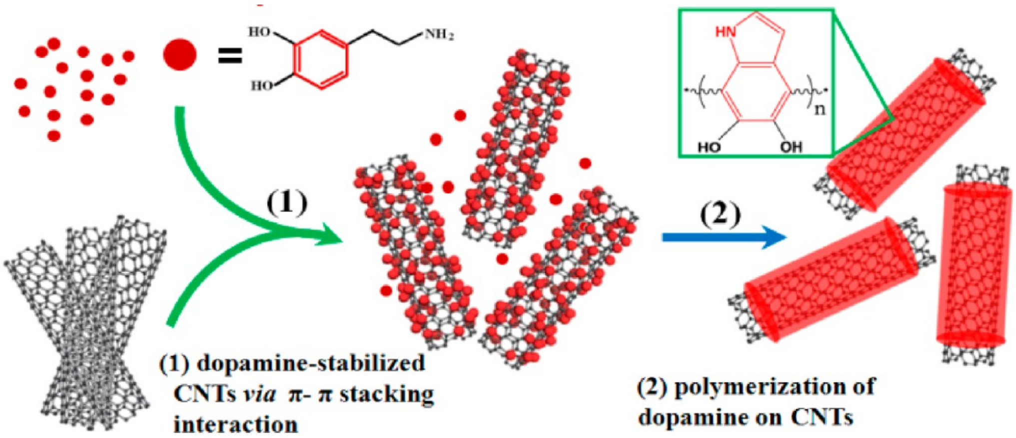
Scheme 1. Synthesis Procedure for Water-Dispersible Polydopamide-Modified MWCNTs



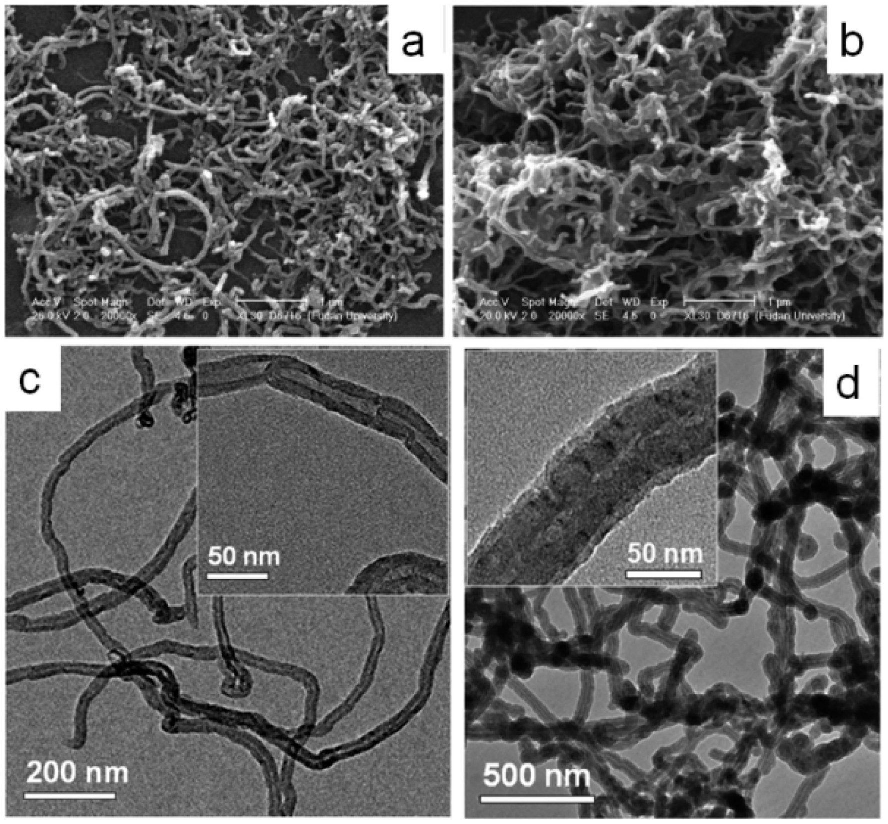


Figure 1. SEM images of (a) MWCNTs and (b) MWCNTs@PDA composites. TEM images of (c) MWCNTs and (d) MWCNTs@PDA composites.

effort has been made to prepare dispersible MWCNTs that can be "soluble" in analyte solutions and further deposited onto the sample target to form a homogeneous layer with the analytes.[23−28] There are two strategies to prepare dispersible MWCNTs: directly oxidizing MWCNTs or coating MWCNTs with a hydrophilic polymer. Pan et al. prepared oxidized MWCNTs by treatment in hot HNO_3 (120 °C, 30 min), and the resulting materials emphasized that a higher degree of oxidation of the MWCNTs resulted in increased dispersibility.[25] However, the oxidized MWCNTs may destroy the structure of the MWCNTs and create many carboxylic groups on its outer surface, which makes it hydrophilic. As a result, the oxidized MWCNTs may lose some of the properties of the pristine MWCNTs, such as their high conductivity and excellent thermal stability. To solve the problem, we developed the method of coating a polymer on the outside of the MWCNTs. In our previous work, we designed MWCNTs@polyaniline composites and applied it as a matrix.[7] The coating with polyaniline increased the dispersibility of the MWCNTs, resulting in its enhanced performance in MALDI-TOF−MS analysis.

Recently, it has been proven that polydopamine (PDA) has an excellent environmental stability, good biocompatibility, and an especially excellent dispersibility in water. Owing to the advantages of PDA, modifying MWCNTs with PDA can make it dispersible and in good combination with analytes. Compared with the oxidized MWCNTs, the coating of MWCNTs with PDA will keep the inherent properties of the pristine MWCNTs without the destruction of its structure. Moreover, PDA can adsorb UV laser energy relative to the oxidative self-polymerization process, which results in a color change of the solution from colorless to deep brown. This property can improve the analysis of MALDI-TOF−MS.[29] Lastly, PDA shells can be easily attached to conjugates with other interesting functionalities, such as modification with Ti^{4+} for the selective enrichment of phosphopeptides,[30] which extends the application of MWCNTs@PDA in biochemistry. Therefore, the synthesis of MWCNTs@PDA for MALDI-TOF−MS analysis is very interesting and important.

In this study, we report a facile modification of MWCNTs through the polymerization of dopamine in an alkaline solution (10 mM Tris, pH 8.5). The synthesis protocol is presented in Scheme 1. First, the dopamine monomer can be adsorbed on the MWCNTs via the $\pi-\pi$ stacking interaction under ultrasonication, improving the dispersibility of the MWCNTs in the aqueous reaction solution. Next, the addition of a small amount of alkaline solution can trigger the oxidative polymerization of dopamine,[31] and a layer of polydopamine can deposit on the surface of pristine MWCNTs at room temperature, leading to the formation of a water-soluble MWCNTs@PDA composite with a core−shell structure (Scheme 1). Compared with the oxidized MWCNTs and other dispersible MWCNTs, MWCNTs@PDA was superiority at keeping the inherent properties of the pristine MWCNTs without the destruction of its structure, adsorbing UV laser energy (which improves the analysis of MALDI-TOF−MS), and further modification with other interesting functionalities that extend the application of MWCNTs@PDA in biochemistry.

The as-synthesized MWCNTs@PDA composites were characterized by different techniques, including electron microscopy (SEM and TEM), Raman spectroscopy, infrared spectroscopy, UV spectroscopy and zeta potentials. Before coating, the pristine MWCNTs have a well-defined morphology with distinct surfaces because of their excellent conductivity and clean surfaces (Figure 1a). By contrast, after coating with PDA, the obtained MWCNTs@PDA composites are somewhat sticky because of the presence of the hydrophilic PDA polymers (Figure 1b), and the sample shows a poor SEM image with bright spots. This phenomenon is attributable to the charge buildup on the sample surface because the PDA polymer has a poor conductivity. TEM images of the MWCNTs before and after coated by PDA are displayed in Figure 1c,d, from which it is clearly visible that a layer of PDA with a thickness of 5 nm has been individually deposited on MWCNTs. No free PDA particles were observed in the TEM image of the MWCNTs@PDA composites sample, which implies that a heterogeneous nucleation of PDA occurred during the solution-phase polymerization process. Because both the dopamine monomers and MWCNTs possess π electrons, the strong $\pi-\pi$ stacking interaction between the aromatic dopamine and the graphitic framework (i.e., sp^2-hybridized carbons) of MWCNTs induce the in situ polymerization of dopamine molecules on the MWCNTs, which makes the MWCNTs disperse well in the solution and helps the homogeneous deposition of PDA polymers on MWCNTs. Therefore, it is due to the unique ambient polymerization of dopamine and the strong interaction between dopamine and MWCNTs that makes it convenient to modify the surface of the MWCNTs.

Fourier transform infrared spectroscopy (FTIR) was employed to characterize both the pristine MWCNTs and MWCNTs@PDA composites (Figure 2). After coating with PDA, many new peaks can be seen in the MWCNTs@PDA composites (Figure 2, curve a). The absorption bands at 3424 and 1624 cm^{-1} can be assigned to the aromatic O−H stretching vibration and the aromatic C═C stretching vibration, respectively. The broad and weak absorption bands in the MWCNTs@PDA spectrum at the range of 1500−1600 cm^{-1} are from the benzene ring structure. The absorption bands between 1400 and 600 cm^{-1} contains the $-CH_2$ bending vibration (1344 cm^{-1}), C−O−H asymmetric bending vibration (1282 cm^{-1}), C−O asymmetric vibration (1240 cm^{-1}), and C−N stretching vibration (1144 cm^{-1}). These results confirm that MWCNTs have been successfully modified by PDA polymers via the simple oxidative-polymerization method. The Raman spectra of pristine MWCNTs and MWCNTs@PDA composites are shown in Figure S1. In the spectrum of MWCNTs, the three strong characteristic peaks at 1336, 1567, and 2678 cm^{-1} are attributed to the D, G, and 2D modes, respectively. The D mode, a disorder-activated Raman mode, is associated with the defects in the sp^3 carbon, graphite sheet, or other impurities.[32] The G mode relates to the movement of two neighboring carbon atoms in the opposite direction of a graphitic sheet.[7] PDA has broad peaks at 1350 and 1600 cm^{-1}, resulting from the stretching and deformation of catechols.[33,34] In the Raman spectrum of MWCNTs@PDA (Figure S1b), all of the characteristic peaks remain at their respective positions, although the peaks are slightly broadened, implying that the Raman spectra of MWCNTs@PDA shows the sum features of MWCNTs and PDA. Moreover, the $\pi-\pi$ interaction between the PDA layer and the walls of MWCNTs may also have some influence on the Raman spectra of MWCNTs@PDA. The results of the measurement from the Raman spectra further confirm that the coating of MWCNTs with PDA polymers through the mild solution-phase polymerization is a non-destructive approach for engineering the surface property of MWCNTs.

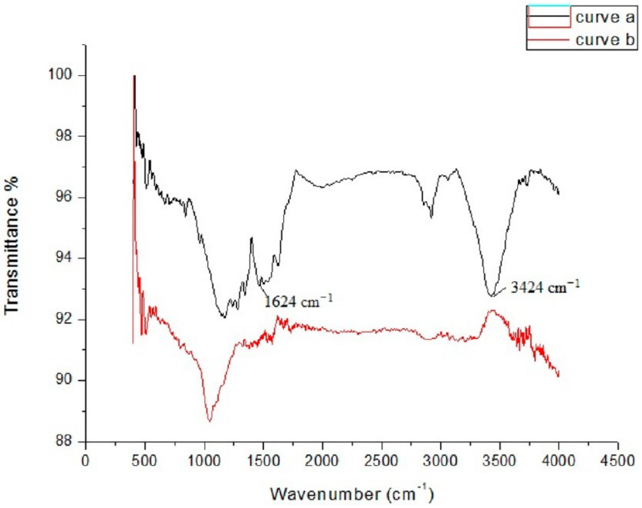


Figure 2. FTIR spectra of MWCNTs@PDA composites (curve a) and MWCNTs (curve b).

UV−vis spectroscopy was used to investigate the capacity of MWCNTs@PDA composites to absorb ultraviolet rays. As shown in Figure S2, the characteristic peak at 268 nm in the UV region of the light spectrum is assigned to the absorption of MWCNTs@PDA, which is attributed to the oxidative self-polymerization process of dopamine into dopachrome and dopa indole. The absorption in the UV region of the

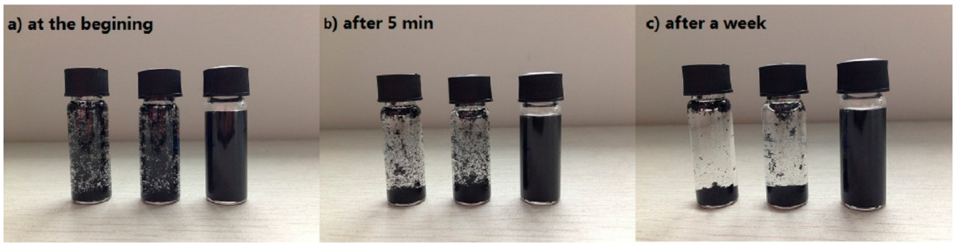


Figure 3. Solubility in water of MWCNTs, MWCNTs treated by HNO_3, and MWCNTs@PDA composites after different periods of time.

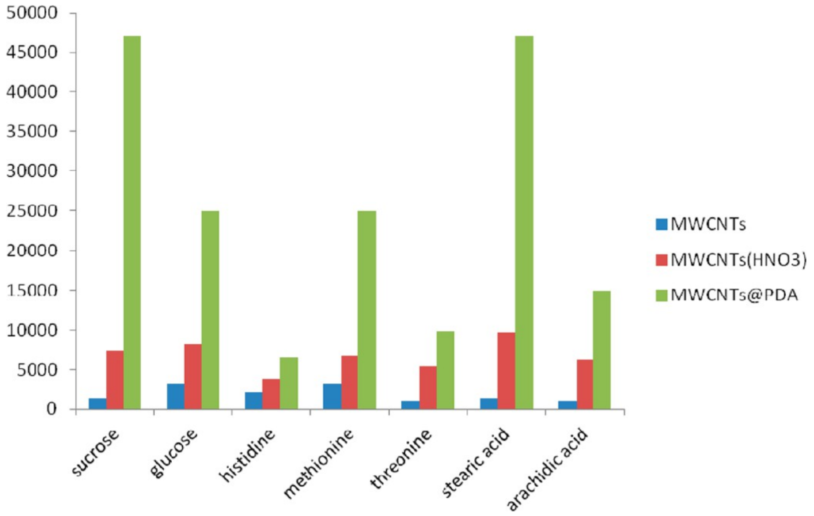


Figure 4. Comparison of the mass peak intensities of various small molecules obtained on different substrates.

MWCNTs@PDA composites make the composites a matrix in the MALDI-TOF−MS technique, which could induce the ionization of the molecules by absorbing and transferring the UV energy to the analytes.

The zeta potentials of the MWCNTs and MWCNTs@PDA composites are shown in Figure S3. As shown in Figure S3, the zeta potential of pristine MWCNTs is −11.9 mV, whereas for MWCNTs@PDA composites, the zeta potential is decreased to −32.4 mV. Moreover, the peak at −11.9 mV that is relevant to MWCNTs cannot be observed after the PDA modification, and only one narrow peak at −32.4 mV is observed for the MWCNTs@PDA composite, which confirms that MWCNTs have been successfully modified by PDA.

To examine the hydrophilic property of MWCNTs@PDA, the pristine MWCNTs, MWCNTs treated by HNO_3, and MWCNTs@PDA composites were dispersed in water separately. After ultrasonicating for 3 min, the samples were allowed to rest for 1 week at room temperature without agitation. As shown in Figure 3, the pristine MWCNTs cannot be dispersed well in water. As time goes by, the pristine MWCNTs and MWCNTs treated by HNO_3 quickly precipitate out of the aqueous dispersion within 5 min; by contrast, the core−shell MWCNTs@PDA composites exhibit excellent water dispersibility because of the presence of numerous hydrophilic moieties, such as hydroxyl and amine groups, even after 1 week. The improved water dispersibility of the MWCNTs@PDA composites makes it an ideal candidate for use as matrix in MALDI-TOF mass spectrometry analyses. Pan et al. prepared oxidized MWCNTs by treatment in hot HNO_3 (120 °C, 30 min), and the resulting materials were dispersed in water for 48 h and remained well dispersed even after centrifugation (5 000 rpm, 10 min), which indicated the excellent dispersibility of the oxidized MWCNTs.[25] However, the oxidized MWCNTs cannot be collected through centrifugation, which will restrict its application in enrichment and other secondary modifications. MWCNTs@PDA composites can be collected through centrifugation, which is beneficial for its application in other fields. Drying a droplet of the dispersion of MWCNTs on a MALDI target can result in significant aggregation of pristine MWCNTs, which become the sweet spot in the analysis (Figure S4a). However, as shown in Figure S4b, after drying the droplet of aqueous dispersion of MWCNTs@PDA on a MALDI plate, a homogeneous and transparent spot can be obtained, which is extremely beneficial to the analysis of water-soluble small molecules.

We evaluated the ability of the MWCNTs@PDA composites to serve as a matrix for the analysis of small molecules in MALDI−MS, with the pristine MWCNTs and MWCNTs treated by HNO_3 also being employed as the matrices under the same conditions for comparison. Various small molecules, such as carbohydrates (sucrose and glucose), amino acids (histidine, threonine, and methionine), and fatty acids (stearic acid and arachidic acid) were selected as samples for MALDI analysis, and all of them were successfully detected with the three above-mentioned matrices, as shown in Figure S5. In the analysis by MALDI−MS, the matrices absorb UV light and transfer the absorbed energy into thermal energy efficiently. The acquired clean mass spectra have low background signals as well as high signal-to-noise (S/N) ratios and peak intensities. Moreover, very few or no fragment ion peaks of the analytes are observed. With the help of the hydrophilic PDA, the MWCNTs@PDA composites can be well dispersed in aqueous solutions and then deposited onto the sample target to form a homogeneous layer with the analytes, which leads to these to

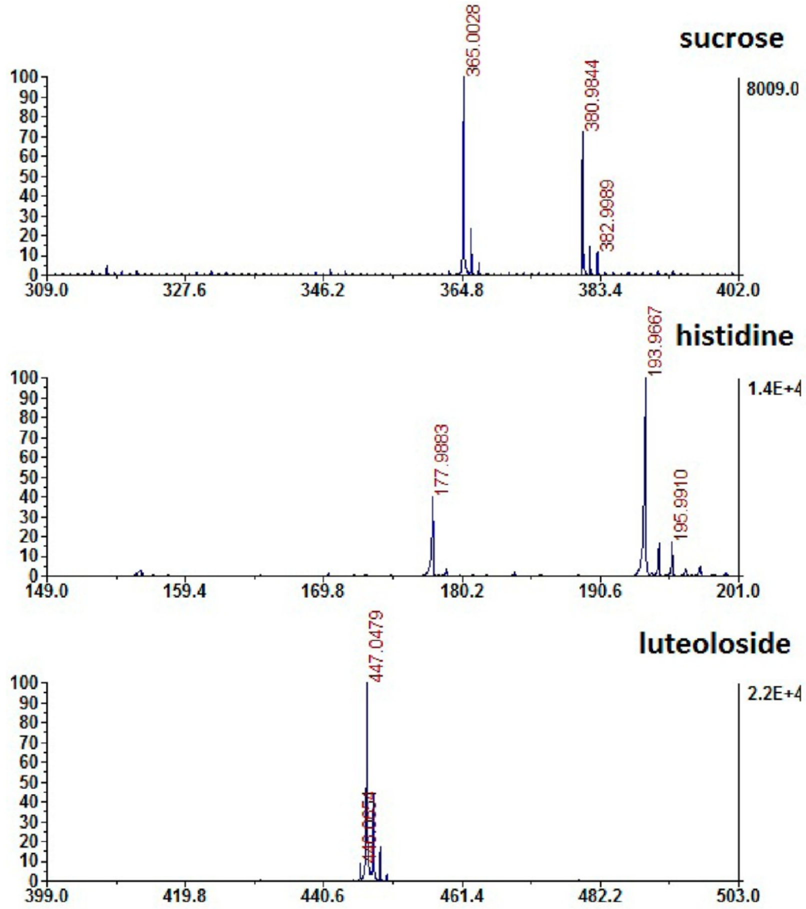


Figure 5. Mass spectra of three different kinds of analytes (sucrose: m/z = 365 $[M + Na]^+$ and 381 $[M + K]^+$; histidine: m/z = 178 $[M + Na]^+$ and 194 $[M + K]^+$; and luteoloside: m/z = 447 $[M - H]^-$) on the matrix of MWCNTs@PDA analyzed by MALDI-TOF−MS.

have the highest peak intensity compared with the other two matrices. The mass peak intensities are summarized for comparison in Figure 4, which further illustrates that the peak intensity of these analyte molecules on the MWCNTs@PDA matrx is higher than that of the other two matrices. Moreover, the abundant electrons in the π-conjugated system could be converted to analytes to assist the ionization of the analyte molecules.[35] The results fully demonstrats that as-synthesized MWCNTs@PDA composites can be a good alternative matrix in the analysis of small molecules by MALDI−MS.

It seems that the interactions between the analytes and MWCNTs@PDA play an important role in the complicated laser desorption/ionization process. We chose sucrose, histidine, and luteoloside (the active compound in traditional Chinese medicine) as analytes to be detected by MALDI-TOF−MS when MWCNTs@PDA was employed as the matrix. Among these three analytes, sucrose has no $\pi-\pi$ interaction with MWCNTs@PDA, histidine has a weak $\pi-\pi$ interaction with MWCNTs@PDA, and luteoloside has a strong $\pi-\pi$ interaction with MWCNTs@PDA. As shown in Figure 5, luteoloside shows the highest peak intensity and sucrose shows the lowest peak intensity in the mass spectra.

Owing to the higher sensitivity of MWCNTs@PDA employed as the matrix in MALDI-TOF to detect small molecules, we evaluated the detection limit of histidine at low concentrations on different matrices, such as pristine MWCNTs, MWCNTs treated by HNO_3, and MWCNTs@PDA, as shown in Figure S6. The sample of histidine was diluted with water at different ratios to obtain concentrations between 1 ng/mL and 0.1 mg/mL for analysis with MALDI-TOF−MS. In the spectra, the sample of histidine can be detected at 1 ng/mL when MWCNTs@PDA composites are employed as the matrix, which is the same as that used by Pan et al. However, when MWCNTs treated by HNO_3 are used as the matrix, the detection limit of histidine is 1 μg/mL, and when the pristine MWCNTs are used as the matrix, the detection limits of histidine is only 10 μg/mL. The results reveal that the MWCNTs@PDA composites have the lowest detection limit compared with pristine MWCNTs and MWCNTs treated by HNO_3. Previous studies have shown that PDA degrades into fragments with a low molecular weight under MALDI-TOF conditions.[36] Importantly, peaks with an m/z ratio of 365 have been reported for pristine PDA. However, in the spectrum of histidine, the matrix-generated noise at m/z = 365 resulting from PDA did not exist. When we synthesized the MWCNTs@PDA composites, the materials were washed by deionized water and ethanol several times, respectively. Moreover, MWCNTs@PDA composites were ultrasonicated for 10 min before centrifugation to remove redundant dopamine or polydopamine that was not polymerized absolutely. Therefore, the composites would not negate the benefits of using MWCNTs for small molecule detection.

The detection sensitivity and reproducibility of employing MWCNTs and MWCNTs@PDA layers as matrix were investigated. We selected methionine as the sample to be detected by MALDI. As shown in Figure S4, the continuous 12 ion mass spectra are obtained from different regions in each spot by applying MWCNTs and MWCNTs@PDA as the matrix, respectively, and the results are illustrated in Figure S7. As shown in Figure S7, the absolute intensities of the mass peaks vary depending on the regions of the spot when the MWCNTs are used, but uniform intensities are obtained wherever the laser spot is applied when the MWCNTs@PDA is used. The results indicate that the MWCNTs@PDA layer shows fewer region-dependent differences in the mass-peak intensities without any requirement for locating the sweet spots (unlike conventional organic matrices, which usually leads to sweet spots because of the many region-dependent differences in the peak intensities resulting from poor mixing and cocrystallization with analytes).[37] The oxidized CNTs for MALDI detection achieved highly reproducible peak intensities (with a relative standard deviation of 5% for the detection of quinine) in the work of Pan et al., which was really a marvelous work and much better than MWCNTs@PDA.[25] Nevertheless, the MWCNTs@PDA composites showed a higher signal intensity and better reproducibility than the pristine MWCNTs did (Figure S7), which illuminated the advantage of PDA coating.

In this work, we successfully synthesized highly water-dispersible polymer-modified carbon nanotubes via a facile oxidative in situ polymerization of dopamine under mild conditions. The obtained MWCNTs@PDA composites possess a hydrophobic MWCNTs core and a uniform hydrophilic PDA shell. By utilizing the capability of the MWCNT component for UV laser irradiation and the water dispersibility of composites, MWCNTs@PDA composites greatly improved their performance as the matrix in MALDI-TOF−MS to analyze small molecules compared with the pristine MWCNTs. The improved performance includes having a higher sensitivity, a facile desorption/ionization process, a higher efficiency in analyte desorption/ionization, and higher peak intensities for the analytes. Because of the low cost and simplicity of the synthesis of MWCNTs@PDA, it is expected that this achievement can contribute to providing a platform for use in the rapid and high throughput MALDI−MS analysis of small molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details, Raman spectra of MWCNTs and MWCNTs@PDA, UV−vis absorption spectra of MWCNTs@PDA, zeta potential distributions of MWCNTs and MWCNTs@PDA, and images of sample plates deposited with MWCNTs and MWCNTs@PDA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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