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# Fabrication of polyaniline/silver composite coating as a dual-functional platform for microextraction and matrix-free laser desorption/ionization

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## ABSTRACT

Polyaniline/silver (PANI/Ag) composites were prepared with a one-step synthesis method, and fabricated into solid-phase microextraction fiber coatings through three different means, i.e. in situ growth, gluing and chemical bonding. This work explored the utility of the as-fabricated PANI/Ag SPME fibers as dual-functional platforms for microextraction and matrix-free laser desorption/ionization (LDI) of the target analyte. The results showed that after incorporating Ag into the PANI polymer, the LDI efficiency was improved by over two times, which was 92.8% the LDI efficiency of the commercial LDI plate. In addition, the in situ grown fiber coatings were observed the most sensitive as dual platforms for the analysis of bifenthrin. The signal intensity was increased over twenty times by using in situ grown fiber, comparing to direct analysis with commercial LDI plate, which were attributed to the excellent extraction ability of PANI backbone, as well as the high LDI efficiency of the PANI/Ag composites. Low detection limit (lower than 10 ng $L^{-1}$) and good fiber-to-fiber repeatability (relative standard deviation 11.0%, n=3) were obtained by using the in situ grown coating for the analysis of bifenthrin, and bifenthrin in real water samples was successfully analyzed. The work successfully coupled SPME with matrix-free LDI, which greatly simplified the analytical process and improved the analytical sensitivity.

## 1. Introduction

The widely applied matrix-assisted laser desorption/ionization (MALDI) technique of co-crystallizing analytes with an organic matrix is restricted for the analysis of small molecules due to the significant background interference in the low mass range ( < 500 Da) [1–9]. To eliminate the matrix ion interference, great endeavors have been devoted to the functional surfaces of sample substrates as ionization platforms, namely, the development of matrix-free LDI technique. It was originally proposed by Sunner and Chen as early as 1995, who utilized the graphite particles with 2–150 µm in size suspended in glycerol to detect a range of peptides [10]. Up to now, a number of functional surfaces made from metal and metal oxide particles [11–17], carbon-based materials [18–25], polymers [26–30], and semi-conducting nanomaterials [31–36], have been reported to work for small molecules analysis. However, considering the complex sample matrices, substantial sample preparation was always required before the LDI detection. Therefore, the development of dual platforms for both sample preparation and matrix-free LDI could probably simplify the analysis procedure and improve the analysis efficiency for the sensitive analysis of small molecules.

Solid-phase microextraction (SPME), which was first introduced in 1990 by Pawliszyn and Arthur, has gained wide acceptance in environmental, food, forensic, clinic fields, etc. for the analysis of different samples, since it provides intriguing advantages of simplicity, speed, sensitivity, low cost, and ease of operation and automation [37–45]. The first combination of SPME with vacuum LDI using polycrystalline graphite as the SPME fiber was reported by Chen et al. in 2002 [46]. However, the absorbed analytes were required to be removed by scraping carbon powder from the graphite surface with matrix liquid. There were several other investigations utilizing sol-gel-derived DHB films [47], DHB-silica particles [48], polypyrrole, or polythiophene [49], as both SPME extraction phases and MALDI substrates for the extraction and LDI analysis of low-mass analytes, such as PAHs and peptides. However, a matrix or a matrix-related coating was still used to aid the ionization of analytes in most works

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[47–51]. And it is still scarce in the literature to combine SPME with matrix-free LDI.

To realize the combination of SPME with matrix-free LDI, it is the crux to develop dual-functional SPME fiber coatings, which is efficient for both extraction and LDI. Polyaniline (PANI) is a widely studied conducting polymer, which possesses good adsorption and energy-transfer abilities because of its highly porous nanostructure, excellent optical and electronic properties [52,53]. Besides, it has been used as a desired sorbent in extraction and microextraction techniques [54–57]. The interaction between PANI and the target analytes attributes to the hydrophobic forces, hydrogen bonding and π-π interaction, making this polymer sensitive for isolation and enrichment of target analytes. Moreover, introduction of metal such as silver, gold, platinum etc., into the polymer matrix is proven to be an easy but effective way to enhance the optical, thermal and electrical properties for widening the application scope offered by each of them individually [58–61]. Among all metals, silver (Ag) exhibits the highest thermal and electrical conductivity. A marked improvement was found in the electrical and thermal conductivities of Ag-PANI composites compared to those of pure PANI (Emeraldine Base), which increased from $10^{-9}$ S $cm^{-1}$ to as high as $10^{3}$ S $cm^{-1}$, and $10^{-1}$ W $m^{-1}$ $K^{-1}$ to $10^{2}$ W $m^{-1}$ $K^{-1}$, respectively [61–64]. Additionally, Ag or Ag-adducts have been successfully employed as inorganic matrices in MALDI technique [14,65–68].

Herein, the PANI/Ag nanocomposites with high specific surface area, strong UV absorbance and favorable conductivity were prepared with a rapid and simple synthesis method, and fabricated into SPME fiber coatings as dual-functional platforms for sample extraction and matrix-free laser desorption/ionization of target analytes.

## 2. Experimental

### 2.1. Chemicals and materials

Ammonium trioxovanadate ($NH_4VO_3$), Dowex Marathon (H) ion-exchange resin, $AgNO_3$, ammonium peroxodisulfate (APS), were all purchased from Sigma-Aldrich (Shanghai, China). Aniline monomer, *o*-xylene, dimethyl formamide (DMF) were obtained from Aladdin (Shanghai, China). High -OH silica optical fibers with core diameters of 660 µm was obtained from Beijing Scitlion Technology CO., LTD (Beijing, China). Neutral silicone glue was bought from Sikasil Ltd. (Guangzhou, China). γ-(2,3-epoxypropoxy)propytrimethoxysilane (GPTMS) was purchased from Alfa Aesar (Shanghai, China). Bifenthrin was obtained from J & K (Beijing, China), and the stock solution (1000 mg $L^{-1}$) was prepared with chromatographic grade methanol. Deionized (DI) water was obtained using Millipore Direct-Q 3 UV water purification system (Merck, Darmstadt, Germany).

### 2.2. Instruments

The laser desorption/ionization (LDI) experiments were performed on an ultrafleXtreme MALDI-TOF/TOF (Bruker Daltonics, Bremen, Germany), equipped with smartbeam™ (355 nm) laser desorption imaging ion source. Each spectrum was acquired from 200 laser shots on a single spot. The range over which ions were detected was $m/z <$ 500. The laser power was adjusted to 100%. The chemical bonding reaction between the as-obtained material and GPMTS was processed in an oven (Binder, Tuttlingen, Germany). The extraction procedures were operated using an MPS autosampler (Gerstel, Mülheim an der Ruhr, Germany).

### 2.3. Pretreatment of SPME optical fibers

The optical fibers were cut into 3.0-cm sections by an optical fiber cleaver. The ends of the optical fibers were polished with a polishing film to make the ends of fibers smooth enough. Then the fibers were sonicated in methanol to remove the coating layer of the optical fibers and expose the fiber cores. After rinsing with DI water, the fibers were treated with 1 M NaOH solution to increase the −OH group on the surfaces of the fibers. After the treatment for 1 h, the fibers were subsequently washed with 1 M HCl solution and DI water. Finally, the optical fibers were dried under ambient conditions and ready for the coating process.

### 2.4. One-step synthesis of PANI/Ag nanocomposites

The synthesis method was mainly based on a previous study reported by Poyraz et al. [69]. The synthesis procedures of PANI and PANI/Ag composites were descried in detail in Text S1 in the Supporting information. Briefly, the PANI particles were synthesized through the oxidative interactions of aniline monomers and $V_2O_5$. Then APS and $AgNO_3$ were added to the system. Herein, APS was acted as both oxidizing agent and catalyst for the polymerization reaction. Simultaneously, the $AgNO_3$ was used as a precursor material for the synthesis of Ag particles. Indeed, different oxidation states of PANI would be obtained with or without the addition of $AgNO_3$ to the reaction solution. The polymerization reactions of aniline to PANI (Pernigraniline Base) and PANI/Ag (Emeraldine Salt) composites were shown in Fig. S1.

### 2.5. Characterization of the as-obtained nanomaterials

The structure and characteristic functional groups of PANI/Ag nanocomposites, as well as PANI nanoparticles were characterized via Fourier transform infrared (FTIR) analysis conducted on a Bruker EQUINOX 55 instrument. The crystalline nature of Ag nanoparticles formed during the synthetic reaction was characterized by powder X-ray diffraction (XRD) analysis, which was performed on an Empyrean powder X-ray diffractometer. The overall morphology images of the as-obtained SPME fibers were analyzed by a JSM-6330F field emission scanning electron microscope (SEM, Japan). In-depth morphological feature of the PANI nanoparticles and PANI/Ag nanocomposites were performed on a FEI Tecnai G2 Spirit high-resolution transmission electron microscope (HR-TEM, FEI Company, Eindhoven, Netherlands) operated at 120 kV. The UV–visible light absorbance spectra of PANI and PANI/Ag were obtained from a UV 3600 spectrophotometer (Shimadzu, Japan).

### 2.6. Fabrication of PANI/Ag-coated fibers

In this work, in-situ grown PANI/Ag-coated SPME fibers were prepared by depositing the pretreated optical fibers in the reactor while the aforementioned one-step polymeric reaction was conducting. Finally, 3-mm long coating was retained and the other coating was scratched off when carrying out the LDI analysis. For preparing the in-situ grown PANI/Ag-coated fibers, a series of the optical fibers were inserted into a large foam block, and then the foam was placed above the reactive solution to make sure that the fiber tips ( > 1 cm) were immersed into the reactive solution. After the reaction was completed, the fibers were taken out and washed with DI water, dried at 150 °C in the oven. A thin black layer could be seen on the surface of the optical fiber. To evaluate and compare the extraction capability of the PANI/Ag-based coatings, two other different types of PANI/Ag-based SPME fibers were prepared by gluing with neutral silicone sealant, and chemical bonding method. The preparation procedures of fiber coatings were all depicted in Fig. 1. And the gluing and chemical bonding methods to fabricate PANI/Ag-coated fibers were described in detail in Text S2 in the Supporting information.

### 2.7. SPME-LDI procedures

Bifenthrin, a widely used pesticide on grain storage but poisonous to human nerve systems, was chosen as the target analyte for the extraction and LDI analysis. The SPME fibers were conditioned at 250 °C in the oven for 30 min prior to use to remove the impurities.