Talanta 181 (2018) 340–345

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Multifunctional Au NPs-polydopamine-polyvinylidene fluoride membrane chips as probe for enrichment and rapid detection of organic contaminants

Saihua Wang[a,b], Hongyun Niu[a], Yaqi Cai[a,b,c,*], Dong Cao[a]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Department of Resources Environmental and Chemical Engineering of Nanchang University, Nanchang, Jiangxi Province 330031, China

ARTICLE INFO

Keywords:
Au NPs-polydopamine-polyvinylidene fluoride membrane chips
Probe
Enrichment
SALDI-TOF MS

ABSTRACT

High-throughput and rapid detection of hazardous compounds in complicated samples is essential for the solution of environmental problems. We have prepared a "pH-paper-like" chip which can rapidly "indicate" the occurrence of organic contaminants just through dipping the chip in water samples for short time followed by fast analysis with surface-assisted laser desorption/ionization time-of-flight mass spectrometry (SALDI-TOF MS). The chips are composed of polyvinylidene fluoride membrane (PVDFM), polydopamine (PDA) film and Au nanoparticles (Au NPs), which are layer-by-layer assembled according to the adhesion, self-polymerization and reduction property of dopamine. In the Au NPs loaded polydopamine-polyvinylidene fluoride membrane (Au NPs-PDA-PVDFM) chips, PVDFM combined with PDA film are responsible for the enrichment of organic analyte through hydrophobic interactions and π–π stacking; Au NPs serve as effective SALDI matrix for the rapid detection of target analyte. After dipping into water solution for minutes, the Au-PDA-PVDFM chips with enriched organic analytes can be detected directly with SALDI-TOF MS. The good solid-phase extraction performance of the PDA-PVDFM components, remarkable matrix effect of the loaded AuNPs, and sensitivity of the SALDI-TOF MS technique ensure excellent sensitivity and reproducibility for the quantification of trace levels of organic contaminants in environmental water samples.

1. Introduction

With the aggravation of the global environmental crisis, it's a great challenge to analyze hazardous chemicals in complicated matrix samples for the sake of environment and human health [1,2]. Conventional methods for analysis of multiple types of organic contaminants mainly rely on mass spectrometry (MS) coupled with gas or high-performance liquid chromatography (GC or HPLC) [3]. Before determination by HPLC-MS or GC-MS, sample pretreatment usually are carried out to purify or extract organic targets from samples with complex matrixes in order to achieve adequate sensitivity for the analysis of low level of organic contaminants. Solid-phase extraction (SPE) and liquid-liquid extraction methods are commonly applied methods for water sample pretreatment. These methods always need large-volume aqueous samples (liter scale) or high amount of toxic organic solvents. After enrichment or extraction, the organic solvents with targets require concentration through evaporation of organic solvent, which may result in loss of some analyte. It's rewarding to develop an alternative method involving fast and environmentally friendly water sample pretreatment combined with direct and sensitive MS detection for the high throughput analysis of organic compounds.

Recently, surface-assisted laser desorption/ionization time-of-flight mass spectrometry (SALDI-TOF MS) technique has exhibited its advantage in easy operation, fast and high throughout analysis of various kinds of organic contaminants in a single run [4–9]. In this technique, nanoparticles serve as the laser desorption/ionization-assisting (LDI) matrix to promote LDI of organic contaminants. Since nanoparticles have strong adsorption ability to organic targets, SPE combined with direct detection with SALDI-TOF MS has been developed in recent years [10–13]. In this method, the nanoparticles demanded to be collected after adsorption by centrifugation or magnetic separation under an external magnetic field, which might lead to loss of nanoparticle adsorbents and poor reproducibility of the results.

In the present study, we immobilized polydopamine (PDA) film and Au nanoparticles on the surface of polyvinylidene fluoride (PVDFM) membrane (Au NPs-PDA-PVDFM). The PDA layer and PVDFM support

---

[*] Corresponding author at: State Key Laboratory of Environmental Chemistry and Ecotoxicology of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
E-mail address: caiyaqi@rcees.ac.cn (Y. Cai).

https://doi.org/10.1016/j.talanta.2018.01.038
Received 18 August 2017; Received in revised form 3 January 2018; Accepted 15 January 2018

can enrich analyte through hydrophobic interactions and π–π stacking; Au NPs are used as an effective SALDI matrix for the rapid detection of target analyte [14–18]. SPE of organic targets is achieved by dipping the membrane in water samples within 1–30 min. Then the membrane with sorbed targets is tested directly using SALDI-TOF MS. Therefore, the concentrations of organic contaminants in water samples can be "read" rapidly and directly. Combined with SPE ability and SALDI matrix function, the Au NPs-PDA-PVDFM membrane can be regarded as a "pH-paper-like" chip to fast "indicate" the occurrence of organic contaminants in water samples. The Au NPs-PDA-PVDFM chip "coupled with" SALDI-TOF MS makes it possible to fast and environmentally friendly pretreat water samples followed with rapid and sensitive detection of organic contaminants.

2. Experimental section

2.1. Chemicals and materials

Hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot 4H_2O$) was supplied by Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China). The 3-hydroxytyramine hydrochloride (dopamine) and tri(hydroxymethyl)-aminomethane (Tris) were obtained from J&K Chemical Ltd. (Beijing, China). Humic acid (HA), bovine serum albumin (BSA), perfluorooctanic sulfonate (PFOS), tetrachlorobisphenol A (TCBPA), tetrabromobisphenol A (TBBPA) and 2, 4, 6-tribromophenol (TBP) were offered by Sigma-Aldrich (Steinheim, Germany). Pentachlorophenol (PCP) was from Dr. Ehrenstorfer (Augsburg, Germany). Chlorinated polyfluoroether sulfonic acids (Cl-PFESA: C8 Cl-PFESA, C10 Cl-PFESA, and C12 Cl-PFESA; the figure represented the number of carbon atoms of the alkyl chain), under the trade name F-53B, were purified from a technical F-53B product purchased from Shanghai Synica Co., Ltd. (Shanghai, China). Ultrapure water was prepared in the lab by using a Milli-Q SP reagent water system (Millipore, Bedford, MA, USA). Polyvinylidene fluoride membrane (pore size of 0.22 μm), mixed cellulose ester membrane (pore size of 0.22 μm) and nylon membrane (pore size of 0.22 μm) were purchased from Jiuding high-tech filtering equipment Co. Ltd., (Beijing, China). The qualitative filter paper was purchased from Hangzhou special paper industry Co. Ltd., (Hangzhou, China).

2.2. Characterization of materials

The morphology of the synthesized membrane was surveyed using a Hitachi S-5500 field-emission scanning electron microscope (FE-SEM, Tokyo, Japan). X-Ray diffraction studies (XRD, PANalytical X′Pert diffractometer, Almelo, Netherlands) were performed using a monochromatized X-ray beam with nickel-filtered Cu Kα radiation and $0.4^\circ\ \text{min}^{-1}$ scan rate. X-Ray photoelectron spectroscopy (XPS) spectra were obtained by a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al Kα radiation (1486.6 eV).

2.3. Preparation of Au NPs-PDA-PVDFM chips

The PVDF membranes were cut into little pieces (about 0.5 × 0.5 cm). To coat polydopamine (PDA) film on the PVDFMs, PVDFMs were firstly immersed in 10 mL of dopamine-Tris solution ($2\ \text{mg mL}^{-1}$, pH = 8.5, 10 mM Tris-HCl buffer), and allowed to proceed for 8 h under stirring at room temperature. The PVDFMs changed from white to light gray. The coated PVDFMs were washed with ultrapure water several times and then soaked into 10 mL $HAuCl_4$ solution (0.4 mM) for 2 h. A pink Au nanoparticles (Au NPs) layer was formed on the PDA film. The Au NPs-PDA-PVDFM was rinsed with ultrapure water and ethanol and dried at room temperature for further use.

2.4. Enrichment and SALDI-TOF MS analysis by Au NPs-PDA-PVDFM chips

When Au NPs-PDA-PVDFM chips was used for enrichment and rapid detection of organic contaminants, the as-prepared Au NPs-PDA-PVDFM chips were immersed in 2 mL sample solution, and the mixture was shaken for few minutes at room temperature. The chips were taken out and dried in air, and then attached onto a MALDI plate for detection.

We also investigated the matrix effect of the Au NPs-PDA-PVDFM chips by attaching the chips on a MALDI plate and spotting 2 μL of the sample solution directly onto the chips followed by air dry for SALDI-TOF MS analysis without above enrichment step.

The LDI-TOF MS was performed on a Bruker Daltonics Autoflex III Smartbean MALDI-TOF mass spectrometer in reflector mode controlled by the FlexControl software. A 337 nm nitrogen laser with a frequency of 100 Hz was used, and the laser power was set to 30%. Mass spectra in negative reflection mode were acquired with 200 laser shots with a LeCroy 9314 digital oscilloscope. All mass spectra were analyzed by Flex Analysis software provided by Bruker Daltonics Corp.

2.5. Analysis of real samples

Tap water, river water and effluent water were used directly for the SALDI-TOF MS analysis without any pretreatment. The Au NPs-PDA-PVDFM chips were immersed in 2 mL of water sample, and the mixture was shaken for 0.5 h at room temperature. The membrane was washed with deionized water gently for 15 s and dried in air at room temperature for the SALDI analysis.

3. Results and discussion

3.1. Preparation and Characterization of Au NPs-PDA-PVDFM chips

The membranes used as supporting material not only can support PDA film and Au NPs, but also affect the enrichment efficiency and SALDI matrix performance of the chips. In a preliminary experiment, mixed cellulose ester membrane, nylon membrane, qualitative filter paper and PVDF membrane were used to prepare the chips. The results showed that mixed cellulose ester membrane was not resistant to organic solvents, and qualitative filter paper was easily broken in the process of preparation and application, so their utilization was greatly limited. As nylon membrane was used as supporting material, a thick PDA film can easily formed on its surface, thus resulting in high density of Au NPs. But too thick PDA and Au NPs brought in stronger background noise and lower MS signals of targets in the analysis of organic contaminants using SALDI-TOF MS. Due to the less dispersion of hydrophobic PVDF membrane in dopamine solution, only a thin PDA film was introduced on PVDF membrane surface, which resulted in suitable density of Au NPs. The coating of PDA film increased the hydrophilicity of PVDF membrane in turn. The hydrophobicity of the PVDF membrane ensured good solid-phase extraction (SPE) performance of the chips. Most importantly, appropriate amount of Au NPs led to perfect matrix effect of the chips in SALDI-TOF MS analysis. All in all, PVDF membranes performed best on the SALDI analysis of target analyte with the advantage of excellent mechanical stability, perfect tolerance of organic solvents, and strong hydrophobic interaction with trace organic contaminants. So PVDF membranes were chosen as support in this follow-up study.

Perfluorooctanesulfonate (PFOS), as a typical perfluorinated compounds (PFCs), is a persistent organic pollutant and has been widespread in the environment. It is very easy to ionize and desorb from the matrix, so we select PFOS as representative to explore the effluence of preparation conditions on the MS signal response. Dopamine modification time affected the thickness of PDA layer, which determined the capacity for Au NPs loading. The signal response increased obviously by