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Electrodeposition of self-assembled poly(3,4-ethylenedioxythiophene) @gold nanoparticles on stainless steel wires for the headspace solid-phase microextraction and gas chromatographic determination of several polycyclic aromatic hydrocarbons

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ABSTRACT

In this work, a novel poly(3,4-ethylenedioxythiophene)@Au nanoparticles (PEDOT@AuNPs) hybrid coating was prepared and characterized. Firstly, the monomer 3,4-ethylenedioxythiophene was self-assembled on AuNPs, and then electropolymerization was performed on a stainless steel wire by cyclic voltammetry. The obtained PEDOT@AuNPs coating was rough and showed cauliflower-like microstructure with thickness of $\sim 40 \mu\text{m}$. It displayed high thermal stability (up to 330°C) and mechanical stability and could be used for at least 160 times of solid phase microextraction (SPME) without decrease of extraction performance. The coating exhibited high extraction capacity for some environmental pollutants (e.g. naphthalene, 2-methylnaphthalene, acenaphthene, fluorene and phenanthrene) due to the hydrophobic interaction between the analytes and PEDOT and the additional physicochemical affinity between polycyclic aromatic hydrocarbons and AuNPs. Through coupling with GC detection, good linearity (correlation coefficients higher than 0.9894), wide linear range ($0.01\text{--}100 \mu\text{g L}^{-1}$), low limits of detection ($2.5\text{--}25 \text{ ng L}^{-1}$) were achieved for these analytes. The reproducibility (defined as RSD) was 1.1–4.0% and 5.8–9.9% for single fiber ($n = 5$) and fiber-to-fiber ($n = 5$), respectively. The SPME-GC method was successfully applied for the determination of three real samples, and the recoveries for standards added were 89.9–106% for lake water, 95.7–112% for rain water and 93.2–109% for soil saturated water, respectively.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants. In the environment they generally come from the incomplete combustion of organic materials and the sources include volcano, forest fire, industrial process, vehicle emission, refinery, incineration and burning tobacco [1]. PAHs exhibit significant hazard to the environment and human health as they have high toxicity, mutagenicity and carcinogenicity. Especially, they are persistent and bioaccumulative, giving rising to their danger. In 2011, EU Regulation 835/2011 established the upper limits for a subset of four specific PAHs in various food matrices [2]. Owing to

the low contents of PAHs in the environmental matrix, enrichment is usually required before their detection.

For their enrichment the most frequently employed technique is solid phase extraction (SPE), generally followed by GC/MS analysis [3–5]. For examples, molecularly imprinted polymers (MIPs) based SPE was used for the detection of PAHs in seawater [6,7]; stir bar sorptive extraction (SBSE) was employed to the analysis of PAHs in soil eluates [8]; air-assisted dispersive micro solid phase extraction (A-d μ -SPE) was applied for the detection of PAHs in biological samples [9]. Solid phase microextraction (SPME) has also been used for the analysis of PAHs [10–13], which is a sensitive technique and usually performed by using a polymer coated fiber [14–17]. But the available commercial fibers, such as polydimethylsiloxane (PDMS), polyacrylate (PA), and polydimethylsiloxane/divinylbenzen (PDMS/DVB), are moderately expensive and fragile, and have limited lifetime at high tempera-

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tures and in organic solvents. In addition, the variety of commercial fibers is rather limited and they lack high selectivity. For these reasons, many researchers focused on developing new fibers with better performance.

In recent years, organic-inorganic hybrid materials have received considerable attention because they can combine the advantages of organic and inorganic materials to some extent [18,19]. Some hybrid materials, especially the hybrid nanomaterials, are considered to be high-efficiency sorbents due to their high specific surface area, and excellent thermal and mechanical stability [20–22]. For instance, Ali et al. prepared a polyaminithiophenol (PATP) with Au coating by layer-by-layer self-assembly for the extraction of PAHs in aqueous solution [23]. It showed excellent properties, but the layer-by-layer self-assembly process was cumbersome and time-consuming. Wu et al. fabricated a poly(3,4-ethylenedioxythiophene)-ionic liquid polymer functionalized multiwalled carbon nanotubes (PEDOT-PIL/MWCNTs) composite coating for the extraction of carbamate pesticides in apple and lettuce samples, which exhibited much higher sensitivity than commercial coatings [24]. In addition, for PEDOT the introduction of conductive nanomaterials benefited the control of its thickness and structure as its conductivity was poor and it tended to crack with its thickness increasing. As we all know, nanoparticles easily aggregate due to high surface energy, high adsorption etc, especially in organic media. PEDOT is one of the few electropolymers that present similar property and structure no matter whether prepared in neutral aqueous solution or in organic media. To the best of our knowledge, there are no reports about the preparation of gold nanoparticles (AuNPs) doped PEDOT coating through electrochemical method in aqueous solution.

In this study, a poly(3,4-ethylenedioxythiophene)@AuNPs (PEDOT@AuNPs) hybrid coating was prepared. Firstly, the monomer 3,4-ethylenedioxythiophene (EDOT) was self-assembled on AuNPs, and then electropolymerization was performed on a stainless steel wire by cyclic voltammetry. The developed fiber demonstrated high selectivity toward PAHs due to hydrophobic interaction and the effect of AuNPs. The organic-inorganic hybrid coating was characterized and its extraction property was explored by using model analytes, including benzenes, phenols, amines and PAHs. The conditions were optimized for the extraction of PAHs, and environmental water samples were determined by coupling with GC.

2. Experimental

2.1. Reagents and materials

All chemicals and reagents were of analytical grade. 3,4-Ethylenedioxythiophene, 3-methylthiophene, 2,2'-bithiophene and chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Trisodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), sodium dodecylbenzenesulfonate (SDBS), sodium chloride (NaCl), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$), potassium hexacyanoferrate(II) ($\text{K}_4[\text{Fe}(\text{CN})_6]$), potassium chloride (KCl), naphthalene (NAP), 2-methylnaphthalene (2-MNAP), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, 1,4-dichlorobenzene, 1,3-dichlorobenzene, *o*-cresol, *p*-cresol, *m*-4-xyleneol, *p*-chlorophenol, aniline, *N*-methylaniline, *m*-methylaniline, *o*-chloroaniline, *m*-chloroaniline, septas and vials came from the Reagent Factory of Shanghai. The stock solution of PAHs (0.10 mg mL^{-1} for all analytes) was prepared with absolute methanol and stored at -4°C .

The water samples were lake water (Sample 1, from East Lake, Wuhan, China) and rain water (Sample 2), they were analyzed with

out any other pretreatment process. Before determination the soil sample was pretreated according to previous report [25]. Briefly, the agricultural soil (1.0 g) was added to a glass bottle, and then 20 mL methanol was added. The bottle was capped and shaken for 24 h. After that, the turbid liquid was centrifuged for 10 min at 5000 rpm and the supernatant was collected for detection.

2.2. Instruments

A CHI 617 A electrochemical workstation (CH Instrument Corp., Shanghai) was employed for preparing SPME fibers. A conventional three-electrode system was adopted, including a stainless steel wire working electrode (0.25 mm, OD), a Pt counter electrode (2.5 cm \times 0.5 mm, OD) and a saturated calomel electrode (SCE) as reference electrode. Electrochemical impedance spectroscopy (EIS) experiment was carried out on a CHI 660 B electrochemical workstation (CH Instrument Corp., Shanghai). The solution used was 0.10 M KCl with 5.0 mM $[\text{Fe}(\text{CN})_6]^{4-}$ and 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-}$. Commercial SPME fiber (100 μm polydimethylsiloxane, PDMS) was supplied by Supelco (Bellefonte, PA, USA).

The analysis of PAHs was performed on a Model SP-6890 gas chromatography instrument fitted with a flame ionization detection (FID) system and a splitless inlet liner (4.6 mm O.D. \times 2.5 mm I.D. \times 110 mm long) (Shandong Lunan Ruihong Chemical Instrument Co., Tengzhou, China). A N2000 chromatographic workstation program (Zhejiang University, Zhejiang, China) was used to process chromatographic data. The separation of samples was carried out on a SE-54 capillary column (30 m \times 0.32 mm I.D.) with 0.5 μm film thickness (Lanzhou Atech Technologies, Lanzhou, China). The stationary phase was polydimethyl phenyl vinyl siloxane (containing 5% phenyl). The following column temperature program was used: 50°C held for 3 min, followed by increasing temperature to 200°C at a rate of $19^\circ\text{C min}^{-1}$, then at a rate of $4.5^\circ\text{C min}^{-1}$ to 240°C , which was held for 2 min; finally it was programmed at 2°C min^{-1} to 250°C , which was held for 2 min. The total run time was 29 min. Hydrogen and air flow rates were maintained at 40 and 400 mL min^{-1} , respectively. Ultrapure nitrogen (99.999%, Xiangyun Chemical Co. Wuhan) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1} . Purge flow rate of N_2 was 8.1 mL min^{-1} and purge time was 45 s. The injection temperature was 280°C . Its inlet was operated under the splitless mode. The FID temperature was set at 280°C . The SPME device was laboratory-made. The scanning electron microscopy (SEM) images were obtained by using an LEO 1530 field emission SEM (Carl Zeiss NTS GmbH, Germany). Transmission electron microscopy (TEM) analysis was performed with a JEM-2100 (200 kV) electron microscopy. The energy dispersive spectroscopy (EDS) was recorded using a Quanta-200 SEM instrument (FEI, The Netherlands).

2.3. Preparation of PEDOT@AuNPs coating on stainless steel wire

AuNPs (diameter: about 14 nm) were prepared by reducing HAuCl_4 using citrate. Briefly, 200 mL 1.0 mM HAuCl_4 solution was heated to boiling, subsequently, 5.0 mL 155 mM trisodium citrate solution was added quickly, resulting in the color changing from pale yellow to deep red. The solution was kept boiling for another 15 min and then cooled down to room temperature, and stored at 4°C .

Fig. 1 shows the preparation process of the PEDOT@AuNPs fiber. Prior to electrodeposition, the stainless steel wire was treated with 1.0 M HNO_3 , 1.0 M sodium hydroxide and distilled water each for 15 min, and then was dried at room temperature. AuNPs aqueous solution (0.50 mM, in terms of HAuCl_4), EDOT (0.050 M) and SDBS (0.060 M) were mixed and let them self-assemble for 12 h. The PEDOT@AuNPs coating was electrodeposited on a stainless steel wire by using CV technique, which was performed between 0 V and

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