A novel coating based on carbon nanotubes/poly-*ortho*-phenylenediamine composite for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons

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ABSTRACT

A novel nanocomposite coating made of poly-*o*-phenylenediamine (PoPD) and oxidized multiwalled carbon nanotubes (MWCNTs) was electrochemically prepared for the first time on stainless steel wire. Subsequently, it was applied to headspace solid-phase microextraction (HS-SPME) and gas chromatographic analysis of biphenyl and seven polycyclic aromatic hydrocarbons (PAHs). The effects of polymerization potential, polymerization time, concentration of *o*-phenylenediamine and oxidized MWCNTs were investigated on the coating process. The fiber coating was carried out easily and in a reproducible manner, and the produced fiber was stable at high temperatures. The surface morphology of the coating was examined by scanning electron microscopy (SEM). The effects of various parameters on the efficiency of HS-SPME process, such as desorption temperature, desorption time, extraction temperature, extraction time and ionic strength were also studied. Under optimized conditions, the calibration graphs were linear in the range of 0.1–300 ng mL^{-1}, and the detection limits for biphenyl and PAHs studied were between 0.02 and 0.09 ng mL^{-1}. The intra-day and inter-day relative standard deviations obtained at 5 ng mL^{-1} concentration level ($n=5$), using a single fiber, were 3.2–7.8% and 5.2–9.3%, respectively. The fiber-to-fiber RSD% ($n=3$) were 6.2–11.3% at 5 ng mL^{-1}. The proposed HS-SPME method was successfully applied for the analysis of PAHs in water samples.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a group of chemicals that were produced during the incomplete burning of fuels, garbage or other organic substances [1]. PAHs can also be found in coal tar, bitumen, crude oil, creosote and roofing tar. Therefore, the distribution of PAHs in the environment is extensive. Since, they were found in soil, air, water, food or household products, the general public may be exposed to PAHs [2–4]. These contaminants are of considerable interest, because some are highly carcinogenic and/or genotoxic in laboratory animals. Some PAHs have been implicated in breast, lung, and colon cancers in humans [5–7]. This is because PAHs bind covalently to DNA, and cause disruptions in its replication. This mechanism, with some modifications, occurs with all carcinogenic PAHs [8]. Therefore, the determination of PAHs in environmental samples is essential.

There are several sample preparation techniques for the determination of these contaminants in the environment. These include: liquid–liquid microextraction [9], solid-phase extraction (SPE) [10,11], stir-bar sorptive extraction (SBSE) [12,13], solid-phase microextraction (SPME) [14–17] and hollow-fiber liquid-phase microextraction [18]. SPME is an extremely attractive alternative to classical extraction methods. It combines sampling, extraction and preconcentration of analytes in a single step. This method enables direct desorption of analytes into the chromatographic systems for analysis. SPME can be applied to both headspace and direct sample analysis with excellent sensitivity and good selectivity [19–21]. However, when volatile compounds or very complex samples are analyzed, headspace solid-phase microextraction (HS-SPME) is preferred.

As SPME greatly depends on sorbent chemistry and coating technology, development of new sorbent materials with improved properties is essential.

In recent years, intrinsically conducting polymers with conjugated double bonds have attracted much attention as advanced materials. They can be easily synthesized through chemical or electrochemical means in both aqueous and non-aqueous media. Electrochemical synthesis is more convenient, because the polymer can be deposited directly on the surface of a metal wire with

better mechanical strength than silica fibers originally used in SPME [22].

Phenylenediamines belong to a class of aniline derivatives having an extra −NH2 group in *ortho-*, *meta-* or *para*-position. *O*-phenylenediamine (oPD) is the most frequently studied member of the group [23]. Poly-*ortho*-phenylenediamine (PoPD) is a widely used permselective polymer in the construction of biosensors for a range of analytes, such as hydrogen peroxide, ascorbic acid, uric acid, acetaminophen and cysteine [24]. PoPD can be deposited electrochemically from *o*-phenylenediamine solutions at neutral pH to produce a thin self-sealing insulating polymer on the electrode surface [25]. The mechanism shown in Scheme 1 has been proposed for the electrochemical growth of PoPD [26]. The monomer is initially oxidized to give the dication radical, which then undergoes chemical coupling to produce a dimer which could be further oxidized. The dication of the dimer could further undergo polymerization to produce a linear chain polymer. Also it can become cyclized to produce a ladder structure through polymerization of the oxidized products.

When the film grows to reach enough thickness to become an insulator covering the electrode surface, further access of monomers to the electrode surface is prohibited. The thickness of PoPD, generated under these conditions, is typically 10–35 nm [25,27]. This is too thin to absorb an adequate amount of analytes, when used as a sorbent in SPME.

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery by Iijima in 1991 [28]. They have been extensively used in a variety of applications. These applications are based on unusual physical or chemical properties of CNTs, such as their highly accessible surface area, excellent electrical conductivity, high mechanical strength and good chemical stability [29]. It has been shown that the introduction of CNTs into a polymer matrix improves electrical, as well as mechanical properties of the original polymer [30,31].

The self-sealing growth of non-conducting polymers, such as poly-*o*-aminophenol is mitigated by using an aqueous suspension of oxidized CNTs as supporting electrolyte during their preparation [32]. The mechanism behind this approach is that, CNTs serve as anionic charge carriers in the liquid phase during electro-
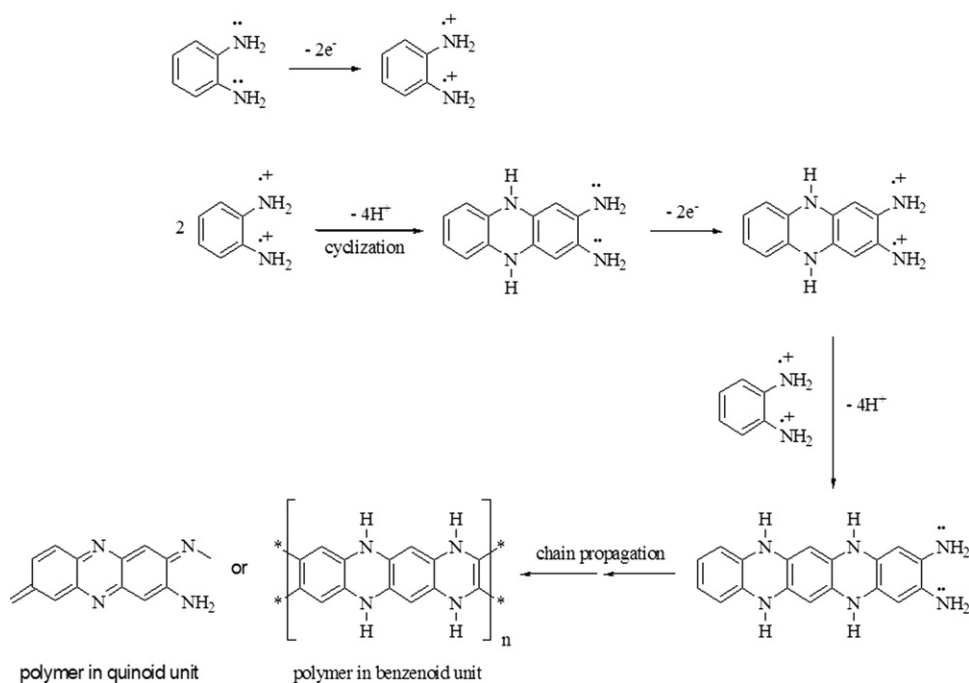
Scheme 1. The mechanism of electrochemical growth of PoPD.
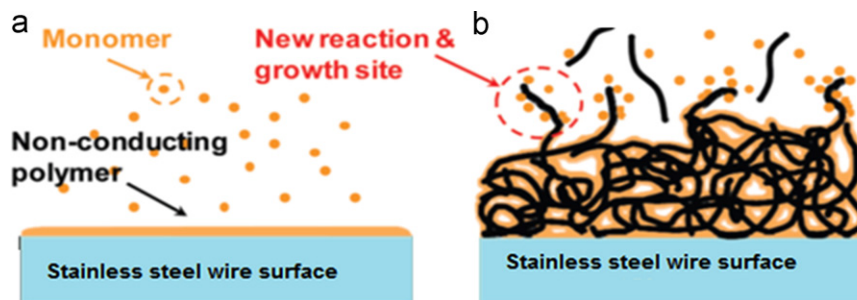

Fig. 1. Schematic diagrams of the steel wire covered with (a) a pure non-conducting polymer layer and (b) a non-conducting polymer/ MWCNTs composite layer on which the interconnected MWCNTs represent the electrode sites where further electropolymerization occurs [32].