Talanta 140 (2015) 29–35

Contents lists available at ScienceDirect

Talanta

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

Facile synthesis of polyaniline-coated SiO_2 nanofiber and its application in enrichment of fluoroquinolones from honey samples

Xiao-Mei He, Gang-Tian Zhu, Hao-Bo Zheng, Sheng-Nan Xu, Bi-Feng Yuan, Yu-Qi Feng [*]

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University,
Wuhan 430072, PR China

ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form
28 February 2015
Accepted 3 March 2015
Available online 10 March 2015

Keywords:
Electrospinning
In-situ polymerization
In-syringe dispersive solid phase extraction
Polyaniline
Fluoroquinolones

ABSTRACT

In this study, polyaniline coated SiO_2 nanofibers (PANI/SiO_2) was prepared by combining electrospinning technique with in-situ polymerization. The proposed strategy for the preparation of PANI/SiO_2 can eliminate the aggregation of PANI and the yield of PANI/SiO_2 was high. Scanning electron microscopy (SEM) images showed that PANI nanoparticles were uniformly coated on the surface of SiO_2 nanofibers. The as-prepared PANI/SiO_2 nanofibers were then applied as the sorbent for in-syringe dispersive solid-phase extraction (dSPE) for the extraction of fluoroquinolones (FQs) from honey samples. The influence of SiO_2 amount on the formation of PANI/SiO_2 and several parameters that affect the extraction efficiency were investigated. Under optimized conditions, a rapid, simple and effective method for the determination of FQs in honey sample was developed by coupling with liquid chromatography-fluorescence detector (LC-FLD) analysis. Due to the fast extraction equilibrium, the whole sample pretreatment process could be accomplished within 4 min. The limits of detection (LODs) for the target FQs were found to be 0.1–1.3 ng/g. The recoveries in honey sample were in the range of 81.4–118.1% with the RSDs of 0.8–14.4% (intra-day) and 1.4–14.9% (inter-day). This study offers a new strategy for the preparation of functional SiO_2 nanofibers using post-electrospinning modification by in-situ polymerization, which could be generally applied in the preparation of various separation materials with electrospun nanofibers.

1. Introduction

Polyaniline (PANI), one of the most popular conductive polymers that possess an extended conjugated π-system associated with the polymer backbone, has attracted great attention in sensors [1,2], solar cells [3,4], electroluminescent devices [5,6], corrosion protection [7,8] and biological applications [9–11]. In addition, PANI is also promising in separation sciences owing to their versatile properties such as hydrophobicity, large π-conjugated structure, polar functional groups, ion exchange property and high stability in water [12–15]. In most previous works, PANI was normally used as packed solid-phase extraction (pSPE) [16–18] sorbent or solid-phase microextraction (SPME) [19–22] coating materials in sample preparation. However, tightly packed PANI particles in SPE mode could result in high back pressure, while limited PANI coating could result in low extraction capacity in SPME mode. Besides, the potential extraction sites are not fully employed due to the aggregation of PANI particles, thus a long extraction time is usually required for pSPE and SPME to reach extraction equilibrium.

To overcome the shortages in SPE and SPME, in-syringe dispersive SPE (dSPE) mode with electrospun fibers as sorbent has been established recently by our group [23]. In-syringe dSPE integrates the advantages of traditional pSPE and dSPE and has some merits, such as low back pressure, fast mass transfer by vortex, easy operation and scale-up. On the other hand, electrospun nanofibers are good candidates for SPE sorbent because of their high surface area, good permeability and flexibility, hierarchically porous structure and easy preparation as membrane that can be conveniently handled and manipulated [24–27]. Unfortunately, PANI is difficult to directly electrospin due to its low molecular weight and low solubility in volatile solvent [28,29]. So far, only the mixtures of PANI with sulfuric acid [30] or other polymers [31–33] have been successfully electrospun. However, the former strategy leads to thick fibers (micrometer-level), and the latter will weaken the PANI properties due to the doping of other polymers.

---

[*] Corresponding author. Tel./fax: +86 27 68755595.
E-mail address: yqfeng@whu.edu.cn (Y.-Q. Feng).

http://dx.doi.org/10.1016/j.talanta.2015.03.006
0039-9140/

In the current work, a novel strategy was developed for the preparation of polyaniline coated SiO_2 nanofibers (PANI/SiO_2) by combining electrospinning and in-situ polymerization. SiO_2 nanofibers were fabricated by eletrospinning according to previous work [34], and then the as-prepared SiO_2 nanofibers were used as template for in situ polymerization of aniline monomers to obtain PANI/SiO_2 nanofibers. PANI nanoparticles could be uniformly dispersed on the surface of SiO_2 nanofibers without aggregation. Furthermore, we used PANI/SiO_2 nanofibers as in-syringe dSPE sorbent for the extraction of fluoroquinolones (FQs) in honey samples followed by determination using high performance liquid chromatography-fluorescence detector (LC-FLD). We anticipate to open up a new way of post-electrospinning modification by in-situ polymerization, especially for polymers those are difficult to electrospin.

2. Experimental

2.1. Reagents and materials

Aniline, ammonium persulfate ($(NH_4)_2S_2O_8$), ethanol, polyvinyl alcohol (PVA, average $M_W \sim 110{,}000$), cetyltrimethylammonium bromide (CTAB), orthophosphoric acid (H_3PO_4, 85 wt% in H_2O), tetraethyl orthosilicate (TEOS) and hydrochloric acid (HCl, 37 wt% in H_2O) were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). HPLC grade acetonitrile (ACN) and methanol was obtained from Fisher Scientific (Pittsburgh, Pennsylvania, USA). Acetone of HPLC grade was obtained from J.T. Baker Chemical Company (Phillipsburg, NJ, USA). Purified water was obtained with a Milli-Q apparatus (Millipore, Bedford, MA, USA). Honey samples were purchased from local markets in Wuhan (China) and stored at 4 °C.

Fluoroquinolones (FQs), including ofloxacin (OFLO), ciprofloxacin hydrochloride (CIP), lomefloxacin (LOM), enrofloxacin (ENRO) and difloxacin hydrochloride (DIF), were purchased from laboratories of Dr. Ehrenstorfer (Augsburg, Germany). Each stock solution of five FQs were prepared in methanol at a concentration of 1 mg mL^{-1} and stored at 4 °C in darkness. Chemical structures of the FQs were shown in Fig. 1.

2.2. Preparation of SiO_2 nanofibers by electrospinning

SiO_2 nanofibers were prepared using electrospinning according to previous work [34] with slight modification. Briefly, 16 g of TEOS was added to the mixture of 5 mL of ethanol and 15 mL of H_2O. Then 0.2 mL of H_3PO_4 was added dropwise to the solution. After stirring for 5 h, 30 g of 7 wt% PVA solution was added into the silica sol to make the viscosity suitable for electrospinning. The resulting mixture was further stirred for 8 h to get a spinnable sol. As for electrospinning process, the sol mixture was loaded into four syringes with uniform diameters of 10.56 mm and driven by a four channels syringe pump with a flow rate of 0.5 mL/h. A grounded aluminum sheet covered with tinfoil served as collector and counter electrode and the distance of tip-to-collector was 15 cm. A high voltage of 15 kV was applied to the needle and a jet was moved and covered on the tinfoil. The fibers were collected and dried at 60 °C for 6 h. Finally, the PVA was removed thoroughly by calcination at 550 °C for 6 h.

2.3. Preparation of polyaniline coated SiO_2 nanofibers (PANI/SiO_2)

The PANI/SiO_2 nanofibrous adsorbent was synthesized by in-situ polymerization of aniline monomers on the surface of the as-prepared SiO_2 nanofibers (Fig. 2a). The polymerization reaction was performed according to the chemical oxidation method described by previous work [35] with some modification. Briefly, 7.45 g of aniline was added into 250 mL of HCl solution (1 M) to obtain aniline solution (0.32 M), and 1 g of SiO_2 nanofibers was dispersed ultrasonically in aniline solution for 3 min. Meanwhile, 4.56 g of $(NH_4)_2S_2O_8$ was added into 250 mL of HCl solution (1 M) to obtain $(NH_4)_2S_2O_8$ solution (0.08 M). Then, $(NH_4)_2S_2O_8$ solution was poured rapidly into aniline solution. After being vigorously stirred for 30 s, the mixture was kept still for 24 h. The product PANI/SiO_2 nanofibers were collected by filtration, and washed with water/ethanol/acetone for several times and vacuum-dried at 60 °C for 8 h. For comparison, pure PANI powder was prepared by the same method except for the addition of SiO_2 nanofibers.

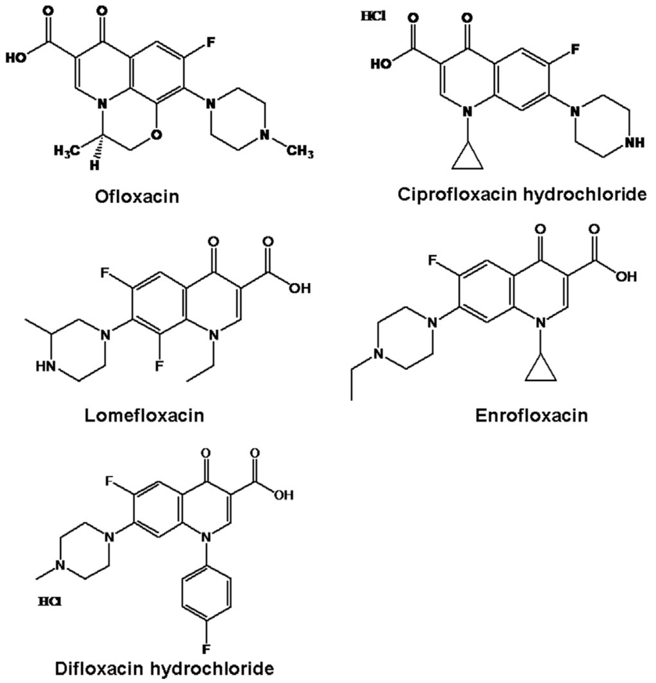

Fig. 1. The chemical structures of FQs.

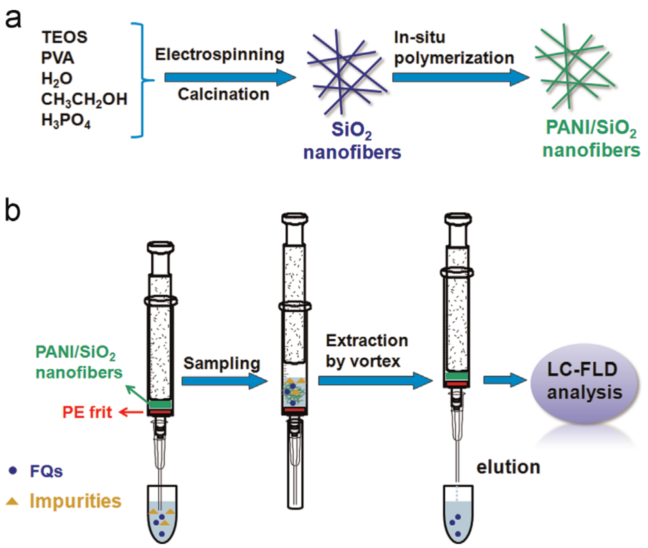

Fig. 2. (a) Schematic diagram of the preparation of PANI/SiO_2 nanofibers. (b) The procedure for the enrichment of FQs with the in-syringe dSPE system.

2.4. Characterization of the prepared materials

Scanning electron microscopy images were taken using Quanta200 scanning electron microscopy (SEM) (FEI, Holland). Nitrogen sorption