



A facile approach for preparation of molecularly imprinted polymers layer on the surface of carbon nanotubes

Xiao-Long Zhang^a, Yan Zhang^a, Xiao-Fei Yin^{b,*}, Bei-Bei Du^b, Cheng Zheng^a, Huang-Hao Yang^{a,b,**}

^a Key Laboratory of Analysis and Detection Technology for Food Safety of the MOE, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian 350002, China

^b The First Institute of Oceanography, SOA, Qingdao 266061, PR China

ARTICLE INFO

Article history:

Received 11 July 2012

Received in revised form

7 October 2012

Accepted 20 October 2012

Available online 9 November 2012

Keywords:

Molecularly imprinted polymers

Carbon nanotubes

9-Vinylanthracene

Theophylline

ABSTRACT

A convenient imprinting method for the preparation of molecularly imprinted polymers (MIPs) layer on the surface of multiwalled carbon nanotubes (MWCNTs) is described. In this method, 9-vinylanthracene was introduced to the surface of MWCNTs, forming vinyl group functionalized MWCNTs. Then the grafting copolymerization of methacrylic acid and trimethylolpropane trimethacrylate in the presence of theophylline as template molecule led to the formation of MIPs-MWCNTs composite. The formation of continuous and nanoscale MIPs layer (thickness about 10–15 nm) would be due to the homogeneous and high-density vinyl groups on the surface of MWCNTs. The resulting surface-imprinted MWCNTs composite showed high binding capacity and good specific recognition behaviour towards template molecule.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Molecular imprinting has become a powerful method for the preparation of artificial biological macromolecular receptors that have the ability to recognize analyte of interest [1–5]. The synthesis of molecularly imprinted polymers (MIPs) involves the formation of a complex of a target molecule (template) with one or more functional monomers through covalent or noncovalent interactions, followed by a polymerization reaction with cross-linking agent. The imprinted molecules are subsequently removed from the polymer, leaving accessible complementary binding sites in the polymeric network. Due to the advantages of MIPs such as stability, ease of preparation, and low cost, MIPs have considerable potential for applications in sensors, catalysis, and separations [6–10].

Among present MIPs, imprinting a matrix with binding sites situated at or near the surface has many advantages: the sites are more accessible, mass transfer and the binding kinetics is faster [5,11,12]. For example, surface-imprinted nanomaterials can be prepared by grafting MIPs to or from the surface of support nanomaterials (e.g., carbon nanotubes [13–16], silica

nanoparticles [12,17–19], magnetite nanoparticles [20–23], quantum dots [24–25] or other substrates [26–28]).

Carbon nanomaterials, which include fullerenes, carbon nanotubes, graphene, carbon nanodots and carbon nanofibers, have received great attention in solid-phase extraction, biosensors and drug delivery due to their unique and promising mechanical, thermal, electronic properties and biocompatibility [29–34]. MIPs grafted on carbon nanomaterials can improve the selectivity of the analytical method based on carbon nanomaterials. Currently, MIPs in conjunction with carbon nanomaterials have widespread applications in sensors [15,35–37] and solid-phase extraction [13–14,38–39]. For example, Kan et al. have prepared vinyl group functionalized multiwalled carbon nanotubes (MWCNTs) that directed selective polymerization of MIPs on the MWCNTs surface [15]. The MIPs can also be grafted onto iniferter-modified MWCNTs and graphene by reversible addition-fragmentation chain transfer (RAFT) polymerization [16,37]. In these works, as to the preparation of the composite of carbon nanomaterials and MIPs, the good interfacial bonding and interactions between carbon nanomaterials and polymers were very important. For example, in order to form uniform MIPs layer on MWCNTs, it is necessary to modify MWCNTs with high-density carboxyl functional groups by strong acid treatment, subsequently obtain vinyl group functionalized MWCNTs via covalent reaction, then the crosslinker and monomer would couple with the vinyl groups on the surface of MWCNTs, forming uniform MIPs layer. Unfunctionalized MWCNTs could not be covered with polymer layer [14–16,36,37].

However, the covalent functionalization of carbon nanotubes always involves strong acid treatments. This treatment has several

* Corresponding author.

** Corresponding author at: Key Laboratory of Analysis and Detection Technology for Food Safety of the MOE, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian 350002, China.

Tel./fax: +86 591 22866135.

E-mail address: hhyang@fio.org.cn (H.-H. Yang).

disadvantages, such as destroying the structure of MWCNTs and consuming time. It is inevitable to disrupt the conjugated π -structure of the carbon nanotubes and lead to adverse changes of its desired optical and electronic properties [40–42]. On the other hand, noncovalent modification of carbon nanotubes using, for example, surfactants, biomolecules, polymers and aromatic molecules, via hydrophobic interactions or π - π stacking for the most part, can do much to preserve their desired properties [42,43]. Hence, it is meaningful to prepare vinyl group functionalized MWCNTs by noncovalent modification.

In this study, we report a facile and versatile approach to noncovalent functionalization of the sidewalls of MWCNTs, namely, the vinyl groups were introduced to the surface of MWCNTs by a simple mixing with 9-vinylanthracene (VA). The anchored molecules of VA on MWCNTs were highly stable against desorption in solvents and the free vinyl groups of anchored VA were available for cross-linking. Then, nanostructured imprinted polymers were prepared by using theophylline as the template molecule, methacrylic acid (MAA) as the monomer, trimethylolpropane trimethacrylate (TRIM) as the cross-linker and 2,2-azobisisobutyronitrile (AIBN) as the initiator.

The resulting MIPs were characterized with transmission electron microscope (TEM), Fourier transform infrared (FT-IR) spectrometer and thermogravimetric analysis (TGA). The adsorption properties were examined by equilibrium rebinding experiments and Scatchard analysis. Two similar structure molecules, caffeine and theobromine, were used to compare the binding performance of imprinted polymers.

2. Experimental

2.1. Reagents and apparatus

MWCNTs were purchased from Chengdu Organic Chemicals Co. Ltd. of Chinese Academy of Sciences. 9-Vinylanthracene (VA) and 2,2'-Azobis(2-methylpropionitrile) (AIBN) were from J&K Scientific Ltd. Theophylline (TH), caffeine, methacrylic acid (MAA), trimethylolpropane trimethacrylate (TRIM) were obtained from Sigma-Aldrich. Theobromine was purchased from Tokyo Chemical Industry Co. Ltd. Other chemicals of analytical reagent grade were obtained from Sinopharm Chemical Reagent Co. Ltd.

Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F20 S-TWIN field emission scanning electron microscope (FEI, USA). The Fourier-transform infrared spectroscopy (FT-IR) spectrum was recorded on a Nicolet 6700 spectrometer (Thermo Electron Corporation, USA). Thermogravimetric analysis (TGA) was conducted on a NETZSCH STA449C instrument from room temperature to 600 °C. Ultraviolet visible (UV-vis) absorption spectra were investigated by a SH-1000 (Lab) spectrometer (Corona Electric, Japan).

2.2. Preparation of MIPs-MWCNTs

MWCNTs (80 mg) were suspended in 20 mL chloroform, and then 16 mg VA was added to the reactor and mixed for 2 h. The monomer (MAA, 1 mmol), template (TH, 0.2 mmol), and the cross-linker (TRIM, 2 mmol) were dissolved by 20 mL of chloroform and well mixed with magnetic stir for 2 h to form a complex of template molecule and functional monomer. The two solutions were mixed before adding the initiator AIBN and the mixture was purged with N_2 . The prepolymerization was first done at 50 °C for 6 h, and the final polymerization was completed at 60 °C for 24 h [12,45]. After reaction, the product was collected by centrifugation and washing twice with methanol. The template was removed by the mixing solvent of methanol and acetic acid (9:1, v/v) repeatedly

until no template could be detected in washing solvent by the UV-vis spectrophotometer (Fig. S1). Non-imprinted reference polymers (NIPs-MWCNTs) were synthesized and treated under the same conditions but without the addition of the template theophylline during the polymerization process.

2.3. Adsorption experiment of MIPs-MWCNTs and NIPs-MWCNTs

The recognition characterization of MIPs-MWCNTs was examined by the adsorption of theophylline from $CHCl_3/ACN$ (9:1, v/v). MIPs-MWCNTs (1 mg) or control NIPs-MWCNTs (1 mg) was suspended in 1.0 mL of theophylline solutions of different concentrations, respectively. The sample was incubated on a rocking table for 2 h at room temperature, then the mixture was centrifuged and the supernatant solution was collected. The concentration of free theophylline in the supernate was measured by UV-vis at 276 nm. The theophylline bound was expressed as the difference between the total mass of theophylline loaded and mass of theophylline in solution after binding. The adsorption dynamics of the MIPs-MWCNTs was performed by analyzing the free theophylline concentration in the supernate at different time intervals. The selectivity of the MIPs-MWCNTs was investigated using caffeine and theobromine as the structurally related compounds.

3. Results and discussion

3.1. Preparation of surface-imprinted MIPs-MWCNTs

Fig. 1 depicts the schematic representation of MIPs-MWCNTs preparation. Vinyl group functionalized MWCNTs facilitates direct polymerization of MIPs on the surface of MWCNTs. So it is important to obtain high-density vinyl group functionalized MWCNTs. The pyrenyl group is known to interact strongly with carbon nanotubes via π - π interaction [44], so we speculate VA could be adsorbed to the sidewalls of MWCNTs. Because of the excellent electronic transference of MWCNTs, the fluorescence intensity of the anchored VA can be quenched efficiently. Therefore, we monitored the VA fluorescence change before and after addition of MWCNTs to verify that VA could be introduced to the surface of MWCNTs. Fig. 2 shows the fluorescence quenching of VA at various concentrations of MWCNTs. The fluorescence intensity at 425 nm and 450 nm (the fluorescent characteristic peaks of VA) decreased with increasing concentration of MWCNTs. This result indicated that VA was adsorbed to the surface of MWCNTs. MWCNTs functionalized with high-density vinyl groups (1.24 mmol g^{-1}) can be obtained through this method and the anchored molecules of VA on MWCNTs were highly stable against desorption. When VA-MWCNTs were re-dispersed in solvents, the fluorescence intensity was stable without increase in a week. These results proved that introducing VA onto the surface of the MWCNTs was an efficient procedure for preparing high-density vinyl group functionalized MWCNTs. Compared with the covalent functionalization of MWCNTs [13–15], which took about 3 days or more to obtain the vinyl group functionalized MWCNTs, this method required only 2 h, one kind of solvent, one-step, under room temperature, which was facile and environment-friendly.

3.2. Characterization of surface-imprinted MIPs-MWCNTs

The crude MWCNTs and MIPs-MWCNTs were characterized with TEM in order to know the surface morphological image. As shown in Fig. 3, crude MWCNTs were in the form of small bundles or individual tubes. Their average size was about 30 nm

Download English Version:

<https://daneshyari.com/en/article/7684146>

Download Persian Version:

<https://daneshyari.com/article/7684146>

[Daneshyari.com](https://daneshyari.com)