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Single-walled carbon nanohorn as new solid-phase extraction adsorbent for determination of 4-nitrophenol in water sample

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ABSTRACT

Single-walled carbon nanohorn (SWCNH) was developed as new adsorbent for solid-phase extraction using 4-nitrophenol as representative. The unique exoteric structures and high surface area of SWCNH allow extracting a large amount of 4-nitrophenol over a short time. Highly sensitive determination of 4-nitrophenol was achieved by linear sweep voltammetry after only 120 s extraction. The calibration plot for 4-nitrophenol determination is linear in the range of 5.0×10^{-8} M–1.0×10^{-5} M under optimum conditions. The detection limit is 1.1×10^{-8} M. The proposed method was successfully employed to determine 4-nitrophenol in lake water samples, and the recoveries of the spiked 4-nitrophenol were excellent (92–106%).

1. Introduction

Solid-phase extraction is the most common technique for preconcentration of analytes, and plays a very important role in modern analytical science. It has the advantages of high recovery, short extraction time, high enrichment factor, low cost, and low consumption of organic solvents over liquid–liquid extraction. Various adsorbents for solid-phase extraction, such as silica-based materials, ion-pair and ion-exchange adsorbents, immunoaffinity extraction adsorbents, nanoparticle-based adsorbents, molecularly imprinted polymers, and various carbonaceous materials, have been used [1–14].

Since the first use of carbonaceous adsorbents for solid-phase extraction in 1980s, various carbon materials have been adopted as solid-phase extraction adsorbents because of their specific properties and high stability [12]. Carbon nanotubes including single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) are novel and interesting materials [15]. Because of their amazing adsorbent effects, carbon nanotubes have been reported as effective solid-phase extraction adsorbents for many analytes such as bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol [16–25]. However, carbon nanotubes have several disadvantages. First, carbon nanotubes especially single-walled carbon nanotubes tend to form big bundles with narrow intertubular gaps, which hinder the permeation and extraction of analytes [25]. Second, it is difficult to remove impurities, which make purified carbon nanotubes expensive. Finally, metal catalyst residues in carbon nanotubes cannot be completely removed. These impurities can affect consequent study and result in controversial results [26,27].

Recently, Iijima's group has reported an intriguing carbon nanomaterial named single-walled carbon nanohorn (SWCNH). SWCNH is synthesized by laser ablation of pure graphite without using metal catalyst with high production rate and high yield, making it potentially cheap [28]. It has been widely used for various applications, such as adsorption, drug delivery, fuel cells, super capacitors, and so on [25,28–35]. It has following distinguishing features. First, SWCNH is horn-shaped single-walled tubule with conical tip. The tubule has a typical diameter of about 2 nm with a length of 30–50 nm. Typically, SWCNH assembles and forms radial aggregates (80–100 nm) with the tips of individual tubules protruding out of the surface of the aggregate. The rough surface structure of the SWCNH aggregates results in weak Van der Waals interactions between aggregates and thus SWCNH has better dispersion in solvents than carbon nanotubes [34]. Second, in contrast to carbon nanotubes, SWCNH has enough large intertubular gaps for permeation of small molecules, ensuring both extremely large surface area and fast extraction. Third, the unique horn-shaped structure of SWCNH results in lots of edge plane graphite and/or defects, and thus the excellent extraction ability. Fourth, through tip opening and assembly of nanohorns, such SWCNH assemblies can provide various accessible pore structures, such as microporosity, mesoporosity, and macroporosity, allowing easy access of both the internal and interstitial spaces of SWCNH. Finally, SWCNH is very pure and essentially metal-free, which avoids cumbersome

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purification and makes it user-friendly. Based on its peculiar features metioned above, SWCNH is promising adsorbent for solid-phase extraction applications.

Phenol and substituted phenols have obtained considerable attention in wastewater and environmental analysis programs due to the human hazards they pose, even at μg/L levels. 4-Nitrophenol can cause significant damages to biodegradation and the human health including methemoglobinemia, the injuries to the liver and kidney. It can also damage the growth of the microbe, animals, and plants. Because of its high toxicity, 4-nitrophenol is included in the US Environmental Protection Agency List of Priority Pollutants [36]. Hence, determination of 4-nitrophenol has attracted much attention [37–41].

In this study, application of SWCNH as solid-phase extraction adsorbent is demonstrated for the first time using 4-nitrophenol as a model analyte. The solid-phase extraction of 4-nitrophenol was monitored by an electrochemical method. Fast solid-phase extraction of organic compounds to SWCNH was shown by effective extraction of 4-nitrophenol within 120 s without taking any special measures, such as applying a suitable potential at the electrodes during extraction or adding suitable dopants. Furthermore, highly sensitive and selective determination of 4-nitrophenol was achieved by the combination of solid-phase extraction to SWCNHs, medium exchange, and linear sweep voltammogram.

2. Experimental section

2.1. Reagents

Professor S. Iijima generously offered dahlia-like SWCNH that was prepared at room temperature by CO_2 laser ablation. MWCNT was purchased from Shenzhen Nanotechnologies Port Co. Ltd. The CAS numbers of chemicals used were as follows: 4-Nitrophenol: 100-02-7; Phenol: 108-95-2; 2-Aminophenol: 95-55-6; 4-Aminophenol: 123-30-8; 2-Nitrophenol: 88-75-5; 3-Nitrophenol: 554-84-7; 2-Chlorophenol: 95-57-8; 4-Chlorophenol: 106-48-9. All chemicals used were of analytical grade purity and used as received. Standard stock solution of 1 mM 4-nitrophenol was prepared by dissolving an appropriate 4-nitrophenol in alcohol/water (*v*/*v*, 1:4) solution. 0.1 M phosphate buffer solutions were employed as supporting electrolyte. All solutions were prepared with doubly distilled water.

2.2. Apparatus

Electrochemical measurements were carried out with the 840B electrochemical workstation (Shanghai, China). A glassy carbon (GC, 3 mm in diameter) electrode, an Ag/AgCl electrode, and a platinum wire were used as working, reference, and counter electrode, respectively. Transmission electron microscopy (TEM) measurements were performed on a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV.

2.3. Preparation of modified GCE

Before each electrode modification, the bare GCE was polished with 0.05 μm alumina slurry to obtain a mirror surface, sonicated in deionized water, and dried with high purity nitrogen stream. 2.5 mg of SWCNH was dispersed in 1 mL dimethylformamide (DMF) with ultrasonic agitation to give a stable suspension, and then 2 μL of the SWCNH solution was dropped onto the GCE surface, dried, and thoroughly rinsed with water to make SWCNH-modified GCE. The MWCNT-modified GCE was prepared by the similar method.

2.4. Analytical procedure

4-Nitrophenol was firstly adsorbed on SWCNH-modified GCE from a 5 mL stirred sample solution for 60 s. Then the SWCNH-modified GCE was transferred into a 5 mL electrolytic blank solution of 0.1 M phosphate buffer. Finally, 4-nitrophenol adsorbed on SWCNH-modified GCE was determined by linear sweep voltammetry with a scan rate of 100 mV/s. After each measurement, the SWCNH-modified GCE underwent successive cyclic voltammetric sweeps between −0.3 V and −1.0 V at 100 mV/s in pH 7.0 phosphate buffer solution to refresh the electrode surface.

3. Results and discussion

3.1. Electrochemistry of 4-nitrophenol following solid-phase extraction

Fig. 1a shows the linear sweep voltammograms in 0.1 M pH 7.0 phosphate buffer solution following 60 s extraction from a 5 mL stirred 1.0×10^{-6} M 4-nitrophenol to SWCNH-modified GCE. A reduction peak appears at −0.71 V and the peak current is 15.72 μA. According to the currently accepted mechanism [40,42], the reduction peak should be attributed to a four-electron transfer reduction of the nitro group (φ-NO_2) to give hydroxylamine derivative.

The extraction of 4-nitrophenol to bare GCE and MWCNT-modified GCE is also investigated for comparison (Fig. 1b and c). A reduction peak at bare GCE and MWCNT-modified GCE appears at −0.67 V and −0.84 V, respectively. The peak current is 0.302 μA at bare GCE while it is 2.81 μA at MWCNT-modified GCE. By comparison, the current response at SWCNH-modified GCE is 51.6 times and 5.55 times larger than that at bare GCE and at MWCNT-modified GCE, respectively. The effective surface area of the working electrode is calculated using $K_3[Fe(CN)_6]$ as probe molecule according to the Randles–Sevcik equation [43]. By comparison, the effective surface area of SWCNH-modified GCE is 1.19 times that of MWCNT-modified GCE (data not shown). Obviously, higher sensitivity at SWCNH-modified GCE is not only attributed to the increase in the surface area but also the excellent extraction ability of SWCNH. The better extraction ability of SWCNH over MWCNT may be attributed to the unique horn-shaped structure of SWCNH [25]. The horn-shaped structure of SWCNH results in the existence of much more edge plane graphite and/or defects, and it is believed that adsorption is strong on edge plane graphite and/or defects [25,44].

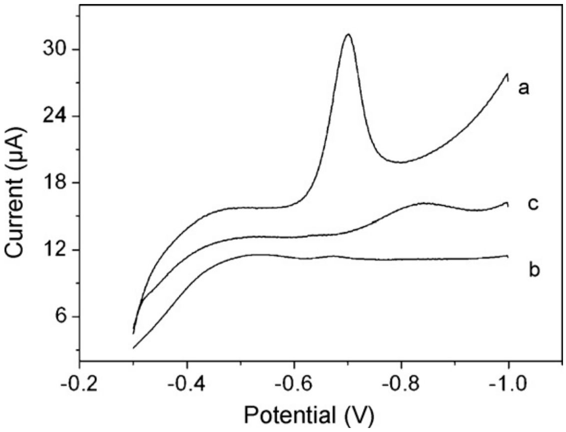

Fig. 1. Linear sweep voltammograms at (a) SWCNH-modified GCE, (b) bare GCE and (c) MWCNT-modified GCE in supporting electrolyte after 60 s extraction from a stirred 0.1 M pH 7.0 phosphate buffer solution containing 1.0×10^{-6} M 4-nitrophenol. Scan rate: 100 mV/s, and supporting electrolyte: 0.1 M pH 7.0 phosphate buffer solution.

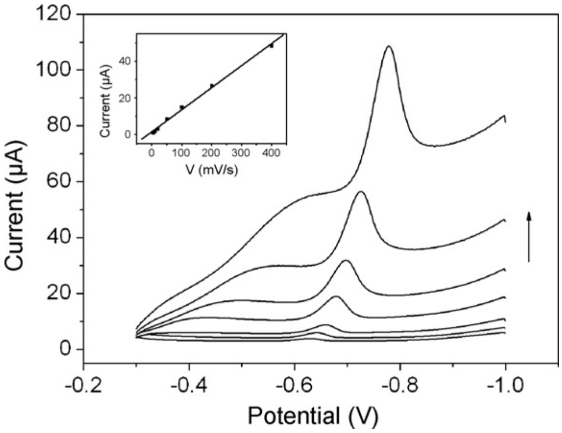

Fig. 2. Linear sweep voltammograms at SWCNH-modified GCE in supporting electrolyte after 60 s extraction from a stirred 0.1 M pH 7.0 phosphate buffer solution containing 1.0×10^{-6} M 4-nitrophenol with different scan rates. Other conditions are the same as in Fig. 1. Inset: influence of scan rates on the peak currents.

Fig. 2 shows the linear sweep voltammograms of the SWCNH-modified GCE at different scan rates ranging from 5 mV/s to 400 mV/s. A negative peak occurred at −0.71 V at a scan rate of 100 mV/s, and the peak potential shifted ~152 mV with increasing scan rate from 5 mV/s to 400 mV/s. A linear relationship can be established between the reduction peak current and the scan rate (Inset of Fig. 2, correlation coefficient = 0.998, $n = 7$) in the range of 5 mV/s to 400 mV/s, indicating that it is a typical surface process.

In this study, a transfer of the working electrode from the sample solution to an electrolytic blank solution was used to improve selectivity [45,46]. Therefore, the sensitivity of the proposed method depended on pH of both the electrolytic blank solution and the sample solution. Fig. 3A shows the effect of pH of the electrolytic blank solution on linear sweep voltammetric detection. The peak potential decreases linearly with pH from 4.0 to 9.0, and the regression equation is: $E_p = -0.0439\ \text{pH} - 0.416$ (Fig. 3B). This implies that the reduction of 4-nitrophenol involves a 1:1 ratio of protons to electrons, and this is in accordance with that reported previously [41,47]. The current response for 4-nitrophenol increases as the pH of the electrolytic solution increases from 4.0 to 7.0, and then decreases at pH higher than 7.0. Consequently, the electrolytic blank solution with a pH of 7.0 was used for further measurement.

3.2. *Optimization of experimental conditions for solid-phase extraction of 4-nitrophenol*

As shown in Fig. 4, the influence of preconcentration time on peak currents is studied. The peak current increases rapidly as preconcentration time increases and levels off at 120 s, indicating that the extraction rate of 4-nitrophenol at SWCNH-modified GCE is quite fast. Fig. 5 shows transmission electron microscope image of the SWCNH-modified GCE. The GCE surface is covered by spherical assemblies made of SWCNH particles whose nanohorn structure has been demonstrated by Iijima et al. [28]. The porosity of the SWCNH film and the large distance between the adjacent SWCNH in the aggregates facilitate rapid and highly effective accumulation of 4-nitrophenol [25].

The pH value of sample solution can influence the form of 4-nitrophenol and therefore can influence the adsorption to SWCNH. So, we investigated the influence of sample pH on the adsorption over the range of 2.0–9.0. As shown in Fig. 6, the response is almost constant and higher than that at other pH when sample pH is in the range of 4.0–7.0. The pka value of 4-nitrophenol is about 7.1. When sample pH < pka (pH 4.0–7.0), the main form of 4-nitrophenol is neutral molecule, which results in a higher affinity of neutral 4-nitrophenol toward SWCNH. At lower pH (pH < 4.0), the surface properties of SWCNH may change and therefore the adsorb ability decreased. At a 4-nitrophenol solution pH higher than 7.0, the main form of 4-nitrophenol is ion, resulting in a lower affinity of 4-nitrophenol toward SWCNH. In view of the optimum pH of the electrolytic blank solution is 7.0, the sample solution of pH 7.0 is used in the following experiments for simplicity.

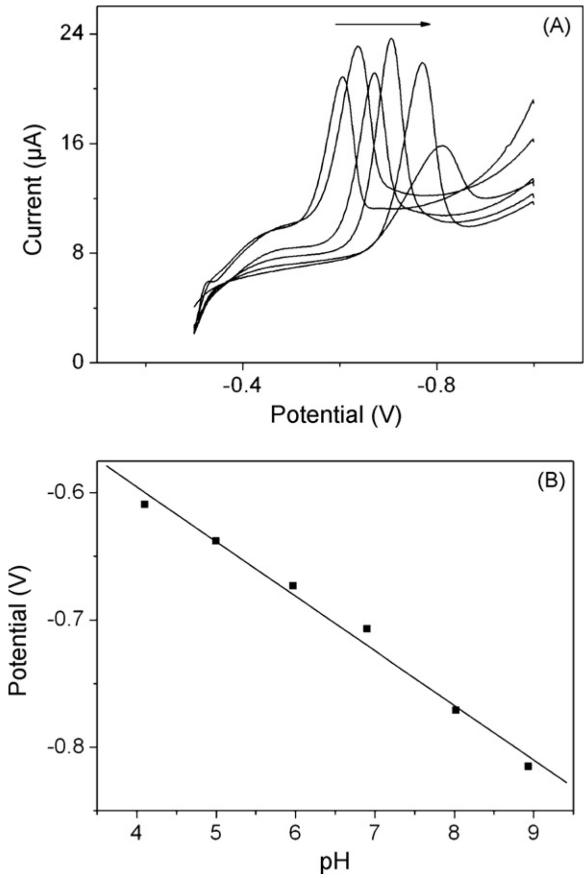

Fig. 3. (A) Linear sweep voltammograms at SWCNH-modified GCE in supporting electrolyte with different pH. From left to right, pH is 4.1, 5.0, 6.0, 6.9, 8.0, and 8.9, respectively. Other conditions are the same as in Fig. 1. (B) Influence of pH of the electrolytic blank solution on the peak potential.

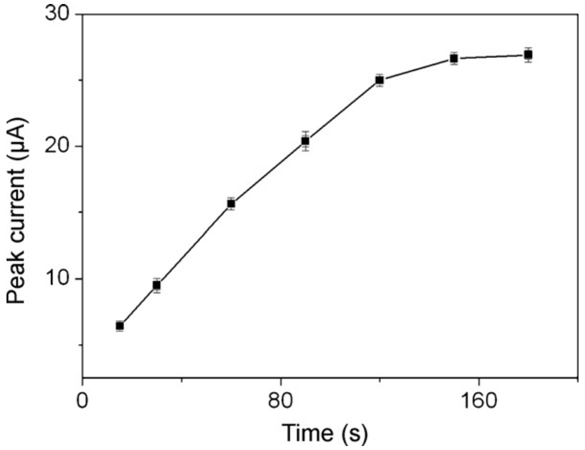

Fig. 4. Influence of extraction time on the peak current of 1.0×10^{-6} M 4-nitrophenol. Other conditions are the same as in Fig. 1. Each point is the average of three measurements.

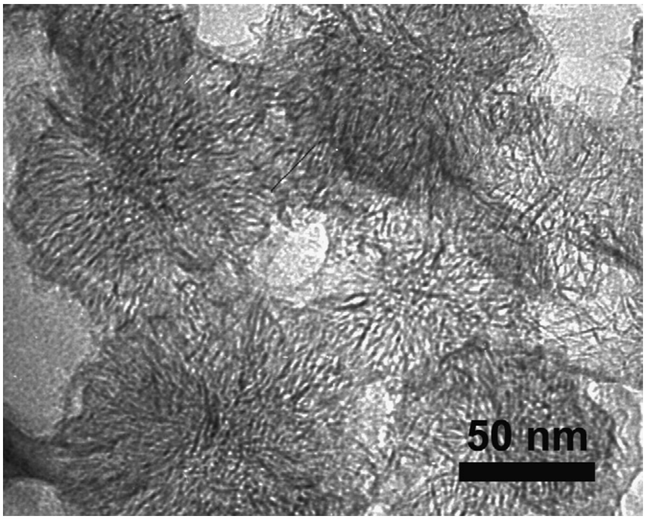

Fig. 5. Transmission electron microscope image of the SWCNH film on GCE surface.

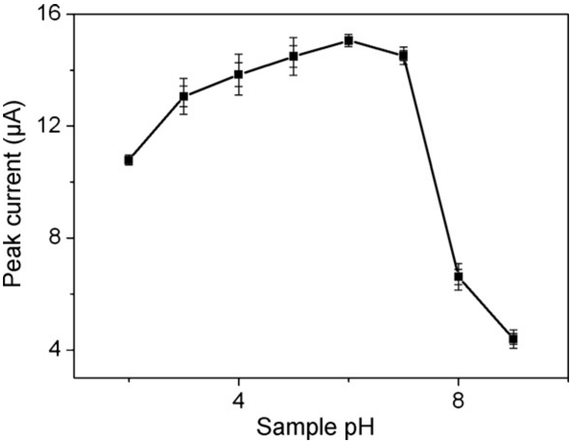

Fig. 6. Influence of pH of 1.0×10^{-6} M 4-nitrophenol solution on the peak current. Other conditions are the same as in Fig. 1. Each point is the average of three measurements.

3.3. Calibration curve

The calibration plot for 4-nitrophenol determination is linear in the range of 5.0×10^{-8} M–1.0×10^{-5} M under optimum conditions (correlation coefficient = 0.999, $n = 12$). The detection limit is 1.1×10^{-8} M and the quantification limit is 3.3×10^{-8} M according to the IUPAC recommendations [48,49]. The relative standard deviation is 4.8% for six consecutive measurements of 1.0×10^{-6} M 4-nitrophenol. The stability of the SWCNH-modified GCE is evaluated by measuring the current response at a fixed 4-nitrophenol concentration of 1.0×10^{-6} M after repeated use. The current response decreases less than 6.6% after 200 times' measurements, indicating that the SWCNH-modified GCE has excellent stability.

3.4. Interference study

The influences of phenol and several phenol derivatives on the 4-nitrophenol signals were tested, and the results were shown in Table 1. The relative standard deviations are less then 4.4% for four successive determinations. Phenol and some substituted phenols did not interfere with the determination of 4-nitrophenol. 2-Nitrophenol and 3-nitrophenol affected determination slightly. Possible interferences of some inorganic species were also evaluated. Most of them showed no interference on the 4-nitrophenol signals with deviations below 5.0%.

Table 1
Influences of inorganic and organic species on the determination of 1.0×10^{-6} M 4-nitrophenol. Extraction time: 60 s, and scan rate: 100 mV/s.

Interference	Concentration (M)	Signal change (%)
Phenol	1.0×10^{-5}	−1.4
2-Aminophenol	1.0×10^{-5}	−3.0
4-Aminophenol	1.0×10^{-5}	−3.0
3-Nitrophenol	1.0×10^{-5}	−7.0
2-Nitrophenol	1.0×10^{-5}	−7.1
2-Chlorophenol	1.0×10^{-5}	−2.6
4-Chlorophenol	1.0×10^{-5}	−3.2
Cd^{2+}	1.0×10^{-5}	−0.5
Co^{2+}	1.0×10^{-5}	+1.7
Ni^{2+}	1.0×10^{-5}	−4.2
Fe^{3+}	1.0×10^{-5}	−3.1
Zn^{2+}	1.0×10^{-5}	−2.2
Mn^{2+}	1.0×10^{-5}	−2.8
Pb^{2+}	1.0×10^{-5}	−4.7
Cl^{-}	1.0×10^{-4}	+1.1
$NO_3{}^{-}$	1.0×10^{-4}	−1.2
$CO_3{}^{2-}$	1.0×10^{-4}	−1.4

3.5. Determination of 4-nitrophenol in lake water sample

In order to evaluate the practical application of this proposed method, it was applied to the detection of 4-nitrophenol in lake water. No signal for 4-nitrophenol was observed when the water samples were analyzed. Thus, the proposed method was applied to detect lake water samples spiked with 4-nitrophenol at a certain concentration. The determination of 4-nitrophenol concentration was performed by the standard addition method. The recoveries of 3.0×10^{-7} M, 9.0×10^{-7} M, and 4.4×10^{-6} M 4-nitrophenol were 92%, 96%, and 106%, respectively.

4. Conclusions

This work shows that SWCNH is excellent solid-phase extraction adsorbent. It can extract 4-nitrophenol rapidly and efficiently. The combination of solid-phase extraction to SWCNH-modified GCE, medium exchange, and linear sweep voltammograms allows fast, sensitive, and selective determination of 4-nitrophenol. Compared with bare GCE and MWCNT-modified GCE, the sensitivity for the determination of 4-nitrophenol at SWCNH-modified GCE increases by 51.6 times and 5.55 times, respectively. Because of its high purity, superior extraction capability, and easily accessible morphology, SWCNH holds great promise for various solid-phase extraction applications.

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