

Three-dimensional carbon nanofiber derived from bacterial cellulose for use in a Nafion matrix on a glassy carbon electrode for simultaneous voltammetric determination of trace levels of Cd(II) and Pb(II)

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Received: 7 January 2017 / Accepted: 10 April 2017 / Published online: 3 May 2017
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Abstract The authors describe the preparation of carbon nanofibers (CNFs) with a three-dimensional network structure by one-step carbonization of bacterial cellulose at 800 °C. The 3D CNFs wrapped with Nafion polymer were cast on a glassy carbon electrode (GCE) which then enables sensitive detection of Cd(II) and Pb(II). Under optimized conditions and at typical stripping peaks of around -0.80 and -0.55 V (vs Ag/AgCl), the electrode exhibits high sensitivity and a wide analytical range of $2\text{--}100\ \mu\text{g}\cdot\text{L}^{-1}$ for both Cd(II) and Pb(II). The detection limits are $0.38\ \mu\text{g}\cdot\text{L}^{-1}$ for Cd(II) and $0.33\ \mu\text{g}\cdot\text{L}^{-1}$ for Pb(II), respectively. The modified GCE was successfully employed to the determination of trace amounts of Cd(II) and Pb(II) in both tap water and waste water.

Electronic supplementary material The online version of this article (doi:10.1007/s00604-017-2260-x) contains supplementary material, which is available to authorized users.

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Keywords Green material · Bacterial fermentation · Freeze drying · Carbon materials · Immobilization · Scanning electron microscopy · X-ray photoelectron spectroscopy · Electroanalysis · Heavy metals · Water analysis

Introduction

Cadmium (Cd) and lead (Pb) are listed as toxic substances by Environmental Protection Agency (EPA), and can induce serious adverse health effects in various organs and tissues, lead to acute or chronic poisoning and even cause cancer [1, 2]. Thus, monitoring trace Pb(II) and Cd(II) is necessary and urgent for the health and safety of humans. Anodic stripping voltammetry (ASV), a kind of sensitive, rapid, and low-cost electrochemical determination method, has been considered as one of the most effective tools for monitoring trace amount of heavy metals in environment [3, 4]. The remarkable sensitivity of ASV depends on an effective accumulation step at the surface of the chemically modified electrode [5]. Therefore, it is a great importance to design electrode materials with good conductivity and ability to achieve this accumulation. Hence, the electrode-modified material is a key factor that strongly affects the electroanalysis performance towards heavy metals [6].

A variety of carbon-based nanomaterials such as graphene [7, 8], carbon nanotube [9, 10] and mesoporous carbon [6, 11], have been used to fabricate the chemically modified electrode due to their high surface area, low charge-transfer resistance and chemical stability [12–14]. Among them, CNF has attracted particular attention owing to its robust mechanical properties, high-volume and corrosion resistance [5, 15]. Some reports on

nanomaterial electrodes modified with CNF, prepared by electrospinning technology have also been reported. Zhao et al. reported that electrospun CNF, prepared by 11 wt% of polyacrylonitrile (PAN) in DMF at high voltage 16 ~ 18 kV, can be applied for simultaneous detection of Cd(II) and Pb(II) by ASV [5]. Guo et al. demonstrated Pd-Ni alloy nanoparticle/CNF, electrospinning of PAN/Pd(acac)₂/Ni(acac)₂, for non-enzymatic analysis of glucose [16]. Although the electrospinning technology can be used for the production of CNF, it still needs toxic and expensive chemical reagents, such as PAN. In this regard, a non-toxic and economic method is desirable for CNF synthesis.

Biomass materials such as bacterial cellulose (BC, (C₆H₁₀O₅)_n), a kind of natural cellulose produced on industrial scales via the microbial fermentation process, have received increasing interest in the fields of both electrocatalysis and electroanalysis [17, 18]. Due to its low cost, renewability and porous nature, BC has been widely considered as a promising precursor for CNF network [19]. To our knowledge, there are only few reports of CNF network derived from BC for electrochemical assay of trace toxic heavy metal ions. Here, we report for the first time that a green CNF network derived from freeze-dried BC is successfully applied for determination of Cd(II) and Pb(II) content in aqueous solutions by using ASV with high sensitivity and selectivity. The resulting data, and a comparison to other relevant systems, shows that CNF is a highly potential candidate for preparing the chemically modified electrode for fast quantification of Pb(II) and Cd(II) in aqueous environmental samples.

Experimental

Chemical reagent and instruments

The pure BC was purchased from Hainan Yeguo Foods Co., Ltd. (Hainan, China, <https://hnyeguo.1688.com/>). 5% Nafion stock solution and 1000 mg·L⁻¹ standard Cd(II) solution were purchased from Sigma-Aldrich (Shanghai, China, <http://www.sigmaaldrich.com/china-mainland/contact-us.html>). Standard Pb(II) solution (1000 mg·L⁻¹) was purchased from NCS Testing Technology Co., Ltd. (Beijing, China, <http://www.ncscrm.com/Member/login.aspx?back=car.aspx>). A 0.1 M acetate buffer (HAc-NaAc) was prepared by mixing the stock solutions of 0.1 M NaAc and HAc. All chemicals are analytical grade and used as received. Ultrapure water (≥18.2 MΩ·cm) was prepared for all electrochemical test solutions.

The morphology of CNF was characterized by a field-emission scanning electron microscope (FE-SEM, Carl Zeiss, Germany). The structure analysis of CNF was made on a transmission electron microscope (TEM, JEOL, Japan) at 200 kV. Surface element and relative chemical valence

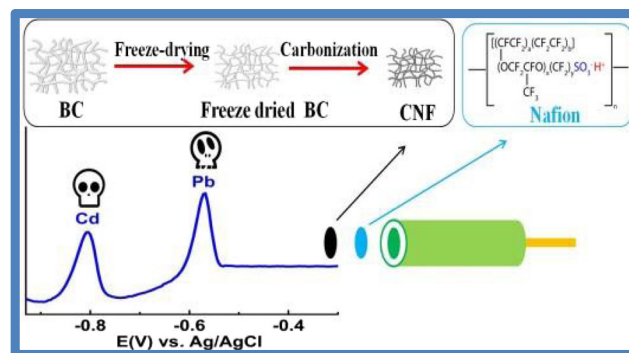
analysis of CNFs was carried out on an X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., UK). The content of Cd(II) and Pb(II) was measured by the inductively coupled plasma-optical emission spectrometry (ICP-OES, VISTA-PRO CCD, Palo Alto, California, USA).

Preparation of CNF and fabrication of CNF-Nafion/GCE

30 g BC was quenched in liquid nitrogen and then freeze-dried for 24 h in order to maintain its vulnerable network according to former report [19]. After freeze-drying, BC was heated up to 800 °C with a rate of 5 °C·min⁻¹ and then kept for 5 h at nitrogen atmosphere. After cooling down to room temperature, a fluffy black substrate was collected and labeled as CNF. Prior to electrode modification, a glassy carbon electrode (GCE, 3 mm in diameter) was carefully polished with 0.3 and 0.05 μm alumina slurry on a polishing cloth, respectively. After that, the electrode was sonicated in ultrapure water and ethanol successively for 5 min, and then dried by flowing N₂. 5 wt% Nafion was diluted to 0.3 wt% with isopropyl alcohol-water (1:4, v/v) solution. Then 3 mg CNF was added in 3 mL of the above solution and further sonicated for 30 min to get homogeneous suspension. Finally, 5 μL suspensions were pipetted and casted on the pretreated GCE surface. After drying for 12 h at room temperature, the CNF-Nafion/GCE was prepared. The preparation procedure of CNF and CNF-Nafion/GCE was illustrated as Scheme 1.

DPASV analysis

The electrochemical measurements were performed on CHI-1040C workstation with a conventional three-electrode cell (bare or modified GCE as working electrode; a Ag/AgCl or saturated calomel electrode (SCE) as reference electrode; a Pt wire as auxiliary electrode) containing 10 mL HAc-NaAc. At first, Cd(II) and Pb(II) in the electrolyte solution were electrochemically reduced and then deposited on the surface of CNF-Nafion/GCE at -1.2 V for 240 s under stirring. Then the solution was kept static for 10 s, and finally, differential pulse



Scheme 1 One-step carbonization preparation of CNFs and fabrication procedure of CNF-Nafion/GCE

voltammetry (DPV) curve was recorded in the potential range from -1.0 V to -0.4 V using amplitude 50 mV, pulse width 50 ms and potential step of a 4 mV.

Results and discussion

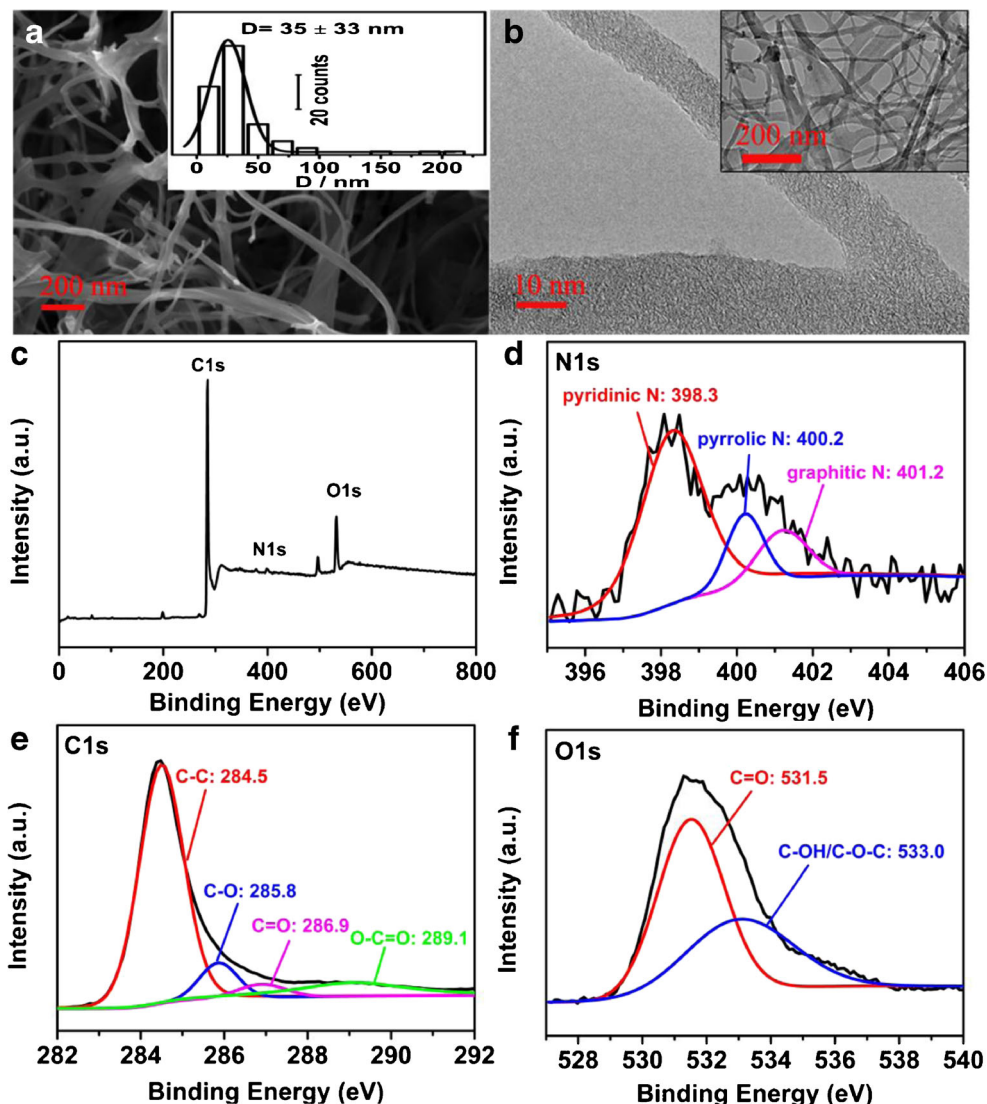
Characterization of CNF

The morphology and structure of the CNF network were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image in Fig. 1a undoubtedly shows the well-connected network of CNF nanowire, which is also confirmed by Fig. 1b inset. The interconnected 3D network structure can expand the specific surface area, shorten the transport pathway of heavy metal ion and accelerate diffusion, which improves electrical analysis heavy metal process [20, 21]. As shown in Fig. 1a inset,

the average diameter of CNF was determined to 35 ± 33 nm with a wide size range from 10 nm to 200 nm. A high magnification TEM image (Fig. 1b) reveals that CNF networks are mostly constructed by amorphous carbon.

To investigate the surface contents and chemical valence of CNF, X-ray photoelectron spectroscopy (XPS) was measured in the energy region from 0 to 900 eV. As shown in Fig. 1c, the XPS survey of CNF exhibits a weak N1s peak around 399.4 eV and two strong peaks representing C1s (284.8 eV) and O1s (532.0 eV) [22]. According to elemental analysis, the content of C, O and N on the CNF surface was 86.3 at%, 9.3 at% and 2.0 at%, respectively. In order to elucidate the detailed configuration, a high resolution N1s spectrum was employed and analyzed in Fig. 1d, revealing that the N in CNF are in the form of pyridinic N (398.3 eV), pyrrolic N (400.2 eV) and graphitic N (401.2 eV) [19, 22]. In the C1s spectrum in Fig. 1e, four peaks are observed and assigned to C-C (284.5 eV), C-O (285.8 eV), C=O (286.9 eV) and O-C=O (289.1 eV) and

Fig. 1 a SEM image (inset: the diameter distribution of CNF) and b HRTEM image of the CNF (inset: LRTEM image); c XPS spectrum of the CNF and high-resolution XPS of N1s d, C1s e and O1s f



O-C = O (289.1 eV) [23, 24]. The core-level XPS spectra of O1s (Fig. 1f) reveals two characteristic oxygen states of C = O (531.5 eV) and C-O (533.0 eV), which are consistent with previous report [25].

Electrochemical characterization

In order to investigate the electrochemical sensitivity of CNF towards Cd(II) and Pb(II), differential pulse anodic stripping voltammetry (DPASV) measurements were carried out on GCE, Nafion/GCE, CNF/GCE and CNF-Nafion/GCE. It can be seen from Fig. 2a that anodic stripping peaks of Cd(II) and Pb(II) are observed for all these four electrodes. The bare GCE presents weak peaks towards both Cd(II) and Pb(II). After casting by Nafion polymer, the electrochemical response signals of both Cd(II) and Pb(II) are improved for the Nafion/GCE, due to the negative anion groups of the polyelectrolyte polymer that favor the statistic accumulation of positive heavy

metal ions [26]. For CNF/GCE, two sharper and more pronounced stripping peaks for Cd(II) and Pb(II) can be observed, attributed to the good conductivity and the efficient ions diffusion in the 3D network structure. Due to the synergistic effect of CNF and Nafion at the GCE, the stripping peaks of Cd(II) and Pb(II) recorded at CNF-Nafion/GCE are much larger than for the other electrodes.

Electrochemical impedance spectroscopy (EIS) is an effective and convenient tool to reveal the interface properties of the electrode materials. It can give information about the impedance changes before and after the electrode modification process. To calculate the electron transfer resistance (R_{ct}), the Randle's equivalent circuit (inset of Fig. 2b) was chosen to fit the impedance data (R_s : ohmic resistance of the electrolyte solution; W : Warburg impedance; C : interfacial capacitance). As seen in Fig. 2b, the CNF modified GCE shows a lower electron transfer resistance of 67Ω , due to the 3D electric conductivity network of CNF. After decorating GCE with

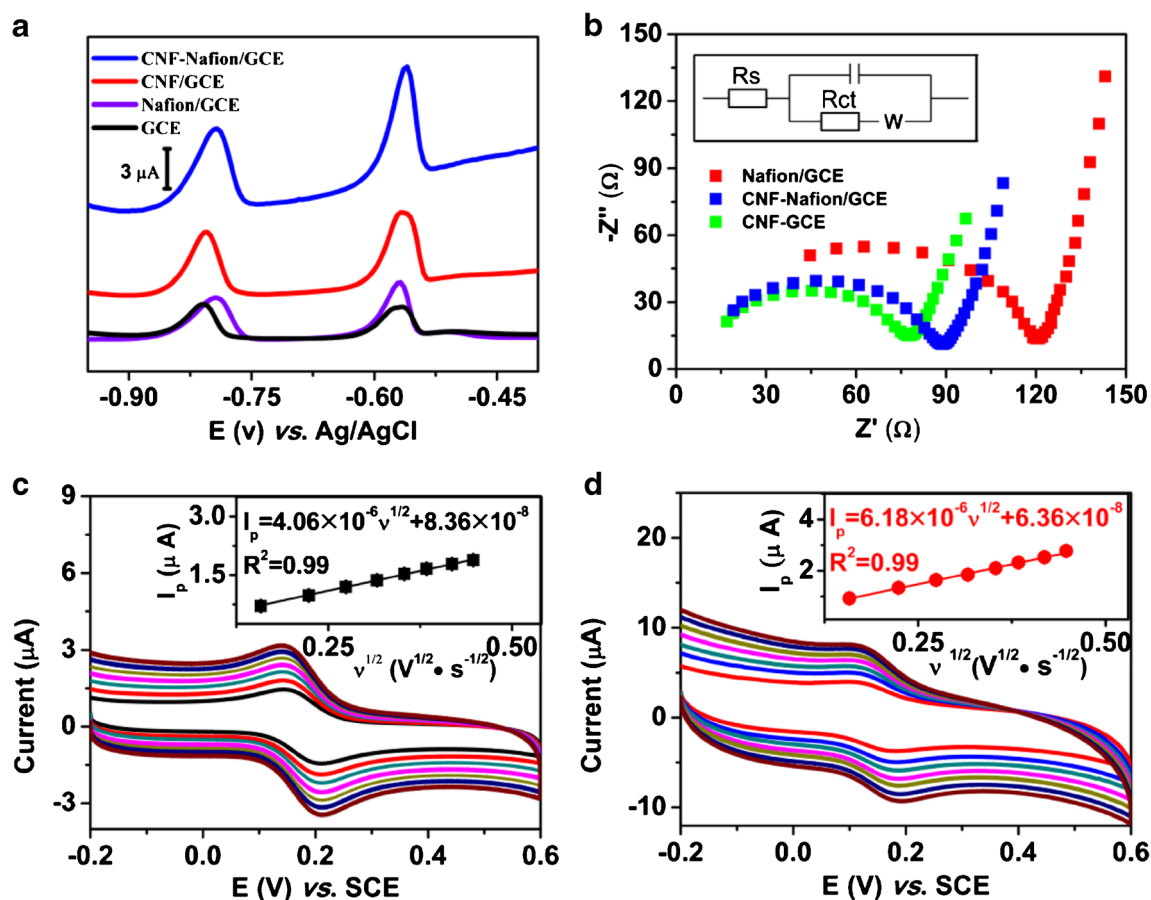


Fig. 2 a DPASV records of bare GCE (black line), Nafion/GCE (purple line), CNF/GCE (red line) and CNF-Nafion/GCE (blue line) in 0.1 M HAc-NaAc buffer (pH 4.5) containing $50 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and $50 \mu\text{g}\cdot\text{L}^{-1}$ Pb(II). b A Nyquist diagram of EIS recorded at CNF/GCE (green square), Nafion/GCE (red square) and CNF-Nafion/GCE (blue square)

in the presence of 0.1 M KCl solution containing 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$. c Cyclic voltammograms of bare GCE and d CNF-Nafion/GCE at various scan rates: 25, 50, 75, 100, 125, 150, 175, 200 $\text{mV}\cdot\text{s}^{-1}$ in 0.1 M KCl containing 0.1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ (inset is relationship between the square of the scan rates and reduction peak currents)

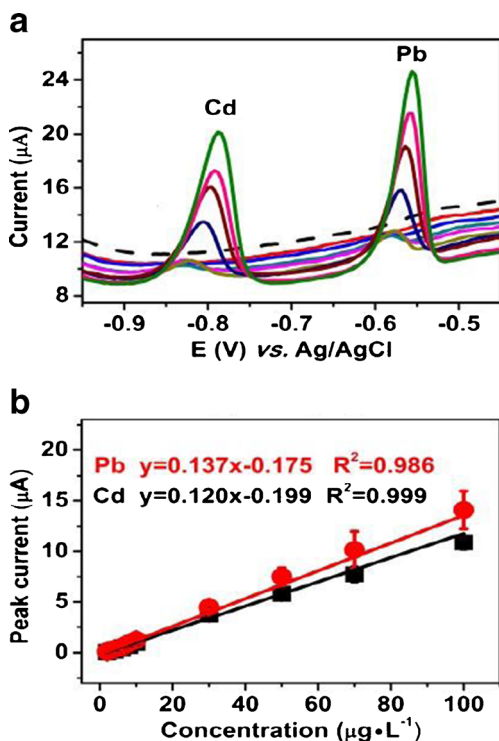


Fig. 3 **a** DPASV curves of CNF-Nafion/GCE in 0.1 M HAc-NaAc with different concentration of Cd(II) and Pb(II) (from bottom to top, 0, 2, 4, 6, 8, 10, 30, 50, 70, 100 $\mu\text{g}\cdot\text{L}^{-1}$, respectively) along with the response to the blank solution (*dash line*). **b** Calibration plot of anodic peak current of CNF-Nafion/GCE as a function of Cd(II) (*black square*) and Pb(II) (*red dot*) concentrations

Nafion, a clear interfacial R_{ct} is observed (108 Ω), indicating the formation of an insulating Nafion layer between GCE surface and the redox probe. When using CNF-Nafion nanocomposite to modify GCE, a moderate value of 76 Ω is obtained for CNF-Nafion/GCE, resulting from the combined action of CNF and Nafion.

To compare with the active surface area of bare GCE and the CNF-Nafion/GCE, cyclic voltammetry with different scan rates was carried out in the presence of 0.1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ containing 0.1 M KCl. The results are presented in Fig. 2c and Fig. 2d. According to the Randles–Ševčík equation, the active surface area of electrode can be evaluated by [27]:

$$I_{pc} = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} c$$

(I_{pc} : the reduction peak current, A; n : the electron transfer number, $n = 1$; A : the effective surface area of the working electrode, cm^2 ; D : the diffusion coefficient, $D = 7.6 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$; ν : scanning speed, $\text{V}\cdot\text{s}^{-1}$; c : the concentration of electrolyte, $c = 1 \times 10^{-7} \text{ mol}\cdot\text{cm}^{-3}$).

The linear dependences of the reduction peak current of bare GCE and CNF-Nafion/GCE versus the square of the scan rates are shown in inset of Fig. 2c and Fig. 2d. The electroactive surface area was calculated to 0.0198 cm^2 for bare GCE and for 0.0302 cm^2 CNF-Nafion/GCE, respectively. The result suggests that CNF-Nafion/GCE exhibits a relatively high electrochemical activity for heavy metals detection, which is ascribed to the great conductivity and pre-accumulation interaction of the CNF-Nafion membrane on GCE.

Electrochemical determination of Cd(II) and Pb(II)

It is well known that Nafion concentration, accumulation time, deposition potential and solution acidity, seriously affect the sensitivity and detection limitation of the CNF-Nafion/GCE towards heavy metal ion detection. Therefore the following parameters were carefully optimized: (a) Nafion concentration; (b) accumulation potential; (c) deposition time; (d) pH. Corresponding data and figures were presented in the Electronic Supporting Material. From Fig. S1, it can be concluded that the best results was

Table 1 Comparison analysis of Cd(II) and Pb(II) determination with literatures

Electrode	Method	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)		LOD ($\mu\text{g}\cdot\text{L}^{-1}$)		Ref.
		Cd	Pb	Cd	Pb	
ElectrospunCNF-Nafion/GCE	ASV	22–112	20.7–103.5	1	0.3	[5]
N-CNT/GCE	SWASV	11–11,200	2–1450	5.6	0.21	[28]
Penicillamine/GCE	ASV	14.3–115.2	10.0–115.1	4.3	3.0	[29]
SPAN ^a /MCM ^b /GCE	SWASV	5–80	5–80	0.7	0.2	[30]
Dendritic Bi/GCE	SWASV	5–50	5–50	0.4	0.1	[31]
GO ^c -DABCC ^d /GCE	DPASV	0.5–25	0.5–25	0.12	0.21	[32]
G ^e -PANI ^f -PS ^g /hSPCE	ASV	10–500	10–500	4.43	3.3	[33]
SNAC ⁱ /GCE	DPASV	10.1–539.6	18.6–1181.0	2.7	1.2	[34]
CNF-Nafion/GCE	DPASV	2–100	2–100	0.38	0.33	This work

^a self-doped polyaniline nanofibers, ^b mesoporous carbon nitride, ^c graphene oxide, ^d 3,8-diaminobenzo cinnoline, ^e grapheme, ^f polyaniline, ^g polystyrene, ^h screen printed carbon electrode, ⁱ spherical carbon nanoparticle decorated activated carbon

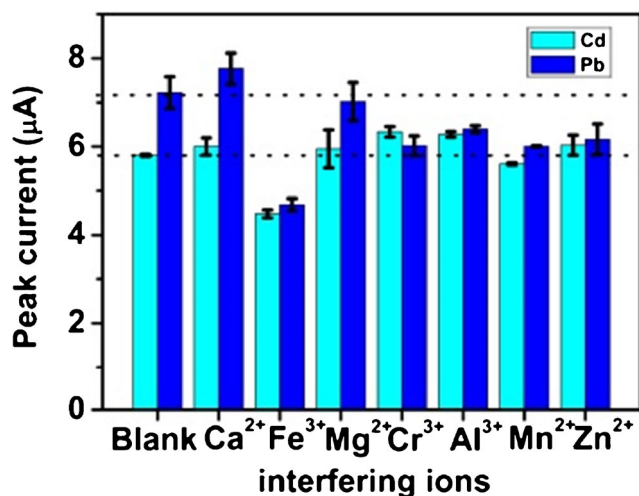


Fig. 4 Selectivity study for the CNF-Nafion modified GCE for determining $50 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and $50 \mu\text{g}\cdot\text{L}^{-1}$ Pb(II) on CNF-Nafion/GCE in the presence of 20-fold excess of various interfering ions

observed for a Nafion concentration of 0.3 wt%, an accumulation potential of -1.2 V, a deposition time of 240 s and a pH of 4.5, respectively.

Under the optimum experimental conditions, the CNF-Nafion/GCE was applied for simultaneous determination of Cd(II) and Pb(II) in 0.1 M HAc-NaAc by DPASV. As presented in Fig. 3a, when the concentrations of Cd(II) and Pb(II) increase synchronously, their peak currents at around -0.80 and -0.55 V increase accordingly. A linear regression equation was calculated in the concentration ranges of 2 – $100 \mu\text{g}\cdot\text{L}^{-1}$ for both Cd(II) and Pb(II). The average data, calculated from the measurements with three different electrodes, allows drawing two linear regressions for Cd(II) and Pb(II) (Fig. 3b). They are described with the following equations:

$$I_p(\mu\text{A}) = 0.120 C_{\text{Cd}}(\mu\text{g}\cdot\text{L}^{-1}) - 0.199 \quad (R^2 = 0.999, N = 3)$$

$$I_p(\mu\text{A}) = 0.137 C_{\text{Pb}}(\mu\text{g}\cdot\text{L}^{-1}) - 0.175 \quad (R^2 = 0.986, N = 3)$$

The limit of detection (LOD) was calculated at a signal-to-noise ratio of three. The estimated values are 0.38 and $0.33 \mu\text{g}\cdot\text{L}^{-1}$ for Cd(II) and Pb(II), respectively.

In Table 1, the performance of the CNF-Nafion/GCE is compared with other materials for the simultaneous determination of Pb(II) and Cd(II). In terms of linear range and a detection limit, the CNF-Nafion/GCE remarkably improves analytical performance towards both Cd(II) and Pb(II).

Selectivity, repeatability and reproducibility of CNF-Nafion/GCE

In respect of selectivity, the interference of other metal ions was investigated in 0.1 M HAc-NaAc containing $50 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and $50 \mu\text{g}\cdot\text{L}^{-1}$ Pb(II) in the presence of 20-fold excess of Ca^{2+} , Mg^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} , Mn^{2+} and Zn^{2+} , respectively. The results are summarized in Fig. 4. It indicates that, except for Fe^{3+} , other metal ions do not lead to serious interference for target heavy metal ion detection, meaning that the CNF-Nafion/GCE exhibits relatively high selectivity for Cd(II) and Pb(II).

The repeatability and reproducibility of the CNF-Nafion/GCE were also evaluated by the electrochemical detection of $50 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and $50 \mu\text{g}\cdot\text{L}^{-1}$ Pb(II). The repeatability of the modified electrode was investigated by using one electrode to detect heavy metal ion concentration for 5 times. Here, the relative standard deviation (RSD) is 5.0% ($N = 5$) for Cd(II) and 3.9% ($N = 5$) for Pb(II), respectively. A similar experiment was performed with five electrodes and the RSD is 5.5% for Cd(II) and 6.2% for Pb(II), implying high reproducibility of the CNF-Nafion modified GCE.

Application to real analysis

For practical applicability, CNF-Nafion/GCE was used to detect Cd(II) and Pb(II) in both tap water and urban waste water. Two kind of water samples were spiked with 10 and $50 \mu\text{g}\cdot\text{L}^{-1}$ for Cd(II) and Pb(II), respectively. Each sample was analyzed three times and the analysis results were listed in Table 2. CNF-Nafion/GCE, with recoveries of 93.0–110.4% for Cd(II) and 90.1–104.6% for Pb(II), which are in good agreement with the values determined by ICP-OES method. It reveals that the CNF-Nafion modified electrode can be

Table 2 Quantitative results of Cd(II) and Pb(II) in real samples with CNF-Nafion/GCE

Sample		Content ($\mu\text{g}\cdot\text{L}^{-1}$)		Added ($\mu\text{g}\cdot\text{L}^{-1}$)		Found ($\mu\text{g}\cdot\text{L}^{-1}$)		Recovery (%)		R.S.D. (% , $n = 3$)		ICP-OES ($\mu\text{g}\cdot\text{L}^{-1}$)	
		Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
Tap water	1	-	-	-	-	-	-	-	-	-	-	-	-
	2	-	-	10	10	9.4	9.6	94.3	97.8	5.4	9.17	9.82	10.11
	3	-	-	50	50	48.6	51.5	97.4	102.4	7.8	9.18	49.31	49.7
Waste water	1	7.5	13.2	-	-	8.3	11.9	110.4	90.1	10.2	4.8	7.40	13.3
	2	7.5	13.2	10	10	17.1	24.3	97.8	104.6	3.0	7.5	16.19	23.53
	3	7.5	13.2	50	50	53.5	58.4	93.0	92.4	1.5	3.7	55.77	62.22

successfully employed to detect Cd(II) and Pb(II) in environmental samples.

Conclusion

In conclusion, a three-dimensional cross-linked carbon nanofiber network derived from bacterial cellulose was prepared by a one-step annealing method. The interconnected network was then wrapped with electronegative Nafion polymer, making the CNF-Nafion modified GCE electrode can expand specific surface area, good ion-diffusion and pre-accumulation ability towards toxic heavy metal ions lead and cadmium. Combining the great conductivity of CNFs and excellent statistical accumulation interaction between Nafion and heavy metal ions, the analytical performance (high sensitivity and low detection limitation) of the CNF-Nafion modified electrode shows that the CNF-Nafion modified electrode is the most potential candidate for the heavy metal analysis in aqueous solution like tap water, industrial waste water, and soil solution after some needful improvements for the aim to completely meet with the strict environmental quality standard.

Acknowledgements This work was supported by National Natural Science Foundation of China (21505154 and 21677171), Xinjiang International Science and Technology Cooperation Project (20166010), 1000-Talent Program (Recruitment Program of Global Expert, In Chinese: Qian-Ren-Ji-Hua), and Project supported by the Special Scientific Research Fund of Agricultural Public Welfare Profession of China (21403014-1). TW acknowledge support from the Artificial Leaf Project Umeå (K&A Wallenberg foundation) and the Swedish Research Council (2013-5252).

Compliance with ethical standards The author(s) declare that they have no competing interests.

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