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A novel flexible carbon nanotube/silver nanowire electrode toward trace Cu(II) detection in water

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Abstract

In this study, a nitrogen-doped multi-walled carbon nanotube (N-MWCNTs)/silver nanowire (AgNWs) nanocomposite electrode was prepared, using polydimethylsiloxane (PDMS) as a flexible substrate and N-MWCNTs and AgNWs as conductive materials. Trace Cu(II) in water was monitored by square wave stripping voltammetry (SWSV). Compared with commercial electrodes, the N-MWCNTs/AgNWs composite electrode generated much higher responsive peak current in detecting Cu(II), due to the enhanced conductivity of the composite electrode and the strong complexing ability of the N-MWCNTs for Cu(II). In the SWSV, this new electrode showed 0.06 µg/L (S/N = 3) limit of detection, a linear range from 0.500 to 100 µg/L, high resistance to interfering metals such as Ca(II), K(I), Zn(II), Na(I), Al(III), Fe(III), Hg(II), Cr(VI), Bi(III), Sb(III) and Sn(II), and stable response in natural water samples without sample pretreatment. This study established a new method for facile fabrication of high-performance flexible Cu(II) sensor with N-MWCNTs and AgNWs.

Keywords Carbon nanotube · Silver nanowire · Nanocomposites · Electrochemistry · Copper detection

Introduction

Heavy metal ion pollution in water causes serious contamination to the environment (Hyder et al. 2022; Liu et al. 2019) and poses great threats to human health (Lee et al. 2016; Witkowska et al. 2021). In order to ensure the quality and safety of the water, real-time online monitoring of heavy metal ion content in the environmental water is highly meaningful. Compared with the conventional detection methods such as flame atomic absorption spectrometry (FAAS) (Molaei et al. 2017), inductively coupled plasma–mass spectrometry (ICP–MS) (Shyam et al. 2021) and flame emission spectroscopy (FES) (He et al. 2020), electrochemical methods have many advantages such as simple operation, low cost, high sensitivity and handiness (Li et al. 2024, 2022, 2023; Ramachandran et al. 2019; Wan et al. 2023; Zhu et al. 2015). Because of these advantages, electrochemistry is easy to realize real-time and online detection. However, conventional ITO, glassy carbon and other solid non-flexible electrodes have many disadvantages such as difficulties in shape customization, fragility and the dependence on

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polishing before use (Bagheri et al. 2021; Ding et al. 2021), which limit their applications in real-time heavy metal detection in water though conventional electrodes were applied in electrochemical sensing (Giacomino et al. 2021; Kokab et al. 2019). In recent years, flexible electrodes have attracted significant attention with the merits in bendability, stretchability, unnecessity for polishing, super-sensitivity and easy fabricability. They can overcome the shortcomings of the traditional solid non-flexible electrodes and are suitable for real-time detection in various conditions (Hui et al. 2020; Zhao et al. 2020). In addition, flexible electrodes allow for promising applications in wearable medical devices (Sun et al. 2022; Yao et al. 2020). Wang et al. prepared a flexible liquid crystal polymer (LCP) sensor by coating LCP with bismuth and Nafion for Cd(II) electrochemical detection with a detection limit of 0.06 µg/L. The low detection limit and the good flexibility of the LCP allowed the sensor to monitor Cd(II) in the actual environment (Nan Wang et al. 2018). Guan et al. prepared a flexible electrode by coating gold nanoparticles on carbon cloth and detected Hg(II) by square wave stripping voltammetry (SWSV) with good reproducibility (Guan et al. 2018).

Both silver nanowires (AgNWs) and carbon nanotubes (CNTs) are conductive materials with nanostructures that have excellent electrochemical properties. AgNWs have good electrical conductivity and nanoeffects (Sun and Du 2019). Our research group have coated AgNWs on the polydimethylsiloxane (PDMS) substrate to fabricate a new flexible silver nanowire electrode (Sun et al. 2020), which has a very sensitive response to metal ions. Using AgNWs coated PDMS as the working electrode, Cu(II) detection was performed with a limit of detection of 0.0927 µg/L and a linear range of 1.00 µg/L–100 µg/L (Yang et al. 2018). CNTs have large surface areas, good adsorption and stable electrochemical properties (Ferrier and Honeychurch 2021; Xia Zhang et al. 2018). Ouyang et al. modified Bi film on carboxylated single-walled CNTs to produce a nanomaterial composite electrode for trace Cr(VI) detection. With a linear range of 0 nM—25 nM and a detection limit of 0.036 nM, the electrode showed high sensitivity and selectivity (Ouyang et al. 2013). For Cu(II) detection, Hui et al. prepared flexible $Ti_3C_2T_x$/MWNTs/PET electrode for monitoring Cu(II) in human biofluids (Hui et al. 2020). Their results showed that Cu(II) could be detected in urine and sweat with linear rages of 10 µg/L – 500 µg/L and 300 µg/L—1500 µg/L, respectively. Although both AgNWs and CNTs have excellent electrochemical properties, there are few reports on using them together as combination nanomaterial electrodes. Furthermore, the field of flexible sensors undergoes fast development and flexible sensors for dynamic applications are highly demanded (Wen et al. 2020; Yuan et al. 2022). Therefore, the development of heavy metal sensors by AgNWs and CNTs on flexible substrate is worth investigation.

In this work, AgNWs and nitrogen-doped multi-walled carbon nanotubes (N-MWCNTs) were uniformly mixed and coated on a PDMS substrate for the preparation of a new flexible N-MWCNTs/AgNWs composite electrode. Nitrogen (N) stands out as an exceptional dopant for chemically enhancing carbon materials due to its comparable atomic dimensions and its five valence electrons, which facilitate robust bond formation with carbon atoms. As a result, N doping enhances the surface energy and reactivity of carbon nanomaterials, promoting charge polarization while minimizing damage to the carbon frameworks (Feng et al. 2011; Jeon et al. 2020; Li et al. 2023). Using the N-MWCNTs/AgNWs electrode as a working electrochemical electrode, trace Cu(II) was successfully detected by SWSV. The results showed that the peak current from the N-MWCNTs/AgNWs composite electrode was higher than that from the AgNWs electrode, which is much sensitive for Cu(II) detection than the AgNPs/RGO electrode and nanoporous gold electrode (Sang et al. 2017; Siepenkoetter et al. 2020), indicating the significant improvement on the sensitivity of the composite electrode by the addition of the N-MWCNTs. The Cu(II) levels in actual water samples were determined by the composite electrode and the recovery rate was 100.8%. Furthermore, our detection method required no pretreatment of the samples, such that real-time and on-site detection could be achieved more conveniently. This study combined two excellent nanomaterials on the flexible electrode by a simple method, which provides a new approach to the preparation of nanocomposite flexible electrodes with excellent performance.

Experimental

Materials and reagents

RTV615 polydimethylsiloxane (PDMS) was purchased from Momentiv (Chino, CA, USA). Silver nanowires (20 mg/mL in ethanol solution, 90 nm in diameter and 60 nm in length) were purchased from XFNANO (Nanjing, Jiangsu, China). Different types of carbon nanotubes, such as nitrogen-doped multi-walled carbon nanotubes (N-MWCNTs), hydroxylated multi-walled short carbon nanotubes (OH-MWCNTs-short), hydroxylated multi-walled long carbon nanotubes (OH-MWCNTs-long) and carboxylated multi-walled carbon nanotubes (COOH—MWCNTs), were also purchased from the XFNANO. Commercial Au (CHI101, diameter = 2 mm) and Ag (CHI103, diameter = 2 mm) electrodes were purchased from CHI (Shanghai, China). Polyvinyl alcohol (PVA) and glycerol (Gly) were obtained from MeilunBio (Dalian, Liaoning, China). Copper chloride, tartaric acid, acetic acid, citric acid and sodium hydroxide were purchased from Sinopharm (Beijing, China). The 4-inch single-side

polished silicon wafer was purchased from Wanxiang Silicon Peak Electronics (Quzhou, Zhejiang, China).

Apparatus

A UV ozone cleaner (Jelight, Model 42 series, USA) was used to clean contaminants on the PDMS surface. Scanning electron microscope (SEM, Hitachi S-4800, Japan) was used to monitor the electrode morphology. SEM-EDS (energy dispersive spectroscopy) analysis was performed with X-MaxN (Horiba, Japan). A CNC router (Multicam, 7000 Series, USA) was used to cut the desired aluminum mold. All electrochemical measurements were taken by a CHI 660e electrochemical workstation (Chenhua Instruments, Shanghai, China).

Preparation of the PDMS substrate

A rectangle-shaped electrode was designed and drawn by the AutoCAD software (Letchumanan et al. 2020). By laser cutting, an aluminum mold with a hollow electrode structure was made. As shown in Fig. 1, a clean silicon wafer was placed under the mold and was tightly fixed by clips. The PDMS solution with a mass ratio of 10:1 was poured into the electrode mold (Xiao Min Zhang et al. 2022). After removing the bubbles, the solid PDMS electrode substrate was obtained by curing at 60 °C for 1.5 h.

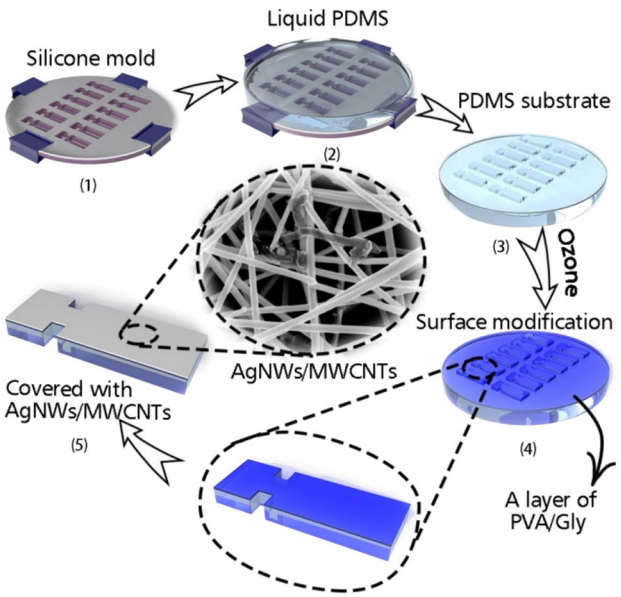

Fig. 1 Schematic of the preparation of the N-MWCNTs/AgNWs flexible composite electrode

Hydrophilic modification of PDMS

As described in our previous work (Jing Sun et al. 2020), the solid PDMS substrate was cleaned with 3 M tape and then by an UV Ozone cleaner. The cleaned PDMS was immersed in a solution of 2% (m/m) PVA and 5% (m/m) Gly for 20 min. After removing the excess liquid, it was vacuum-dried at 60 ℃ for 2 h. The above steps were repeated three times, and finally, the dried PDMS was vacuum heated at 100 ℃ for 20 min to obtain a stable hydrophilic surface.

Preparation of N-MWCNTs/AgNWs flexible electrode

1 mg/mL of N-MWCNTs was prepared using ultrapure water as the solvent. AgNWs solution of 2 mg/mL was prepared with a mixture of ethanol and water (1:1, v/v). 10 µL of the N-MWCNTs solution and 50 µL of the AgNWs solution were mixed evenly, and the mixture was coated on the hydrophilic-modified PDMS surface uniformly. The N-MWCNTs/AgNWs flexible electrode was ready to use after drying at room temperature for one day.

Electrochemical detection of Cu(II)

A three-electrode system consisting of N-MWCNTs/AgNWs working electrode, Ag/AgCl reference electrode (3 mol/L KCl) and Pt counter electrode was used for Cu(II) detection. Different concentrations of Cu(II) solution were prepared with 0.5 mg/L Bi(III) and 0.1 mol/L tartaric acid–sodium tartrate buffer solution. The final pH of each Cu(II) solution was adjusted to 3.8 by the addition of sodium hydroxide. SWSV was used to record the current response of Cu(II) in a potential range of − 0.3 V–0.25 V with deposition potential of − 1.0 V and deposition time of 300 s. Standard curves of the current responses by the N-MWCNTs/AgNWs electrode against the Cu(II) concentrations were calculated by Origin 2019b (OriginLab, Northampton, MA, USA). Water samples from a lake on our campus and tap water were measured under the optimized conditions.

Electrochemical active surface area (ECSA) was calculated using the following equation (Jing Sun et al. 2019).

$$\mathrm{ECSA} = \frac{Q}{sl}$$

where Q is the coulombic charge of the AgO reduction peak, s is the proportional constant (280 µC cm^{-2}) of the area dependent charge and l (g cm^{-2}) is the loading of the electrocatalyst Ag.

Results and discussion

Morphological and conductivity characterization

The morphology of the N-MWCNTs/AgNWs composite electrode was characterized by SEM (Fig. 2a). N-MWCNTs and AgNWs were evenly distributed on the surface of the flexible electrode, and a 3D network was formed. The AgNWs connected to each other and the N-MWCNTs scattered in the network. The SEM image of the AgNWs electrode is shown in Fig. 2b for comparison. EDS analysis demonstrated the element compositions of the composite electrode, mainly by C and Ag, reflecting the contribution of N-MWCNTs and AgNWs, respectively, while the Si and O in the EDS were from the substrate PDMS (Fig. 2c). The average sheet resistance of the N-MWCNTs/AgNWs composite electrode was 0.457 Ω/sq. In comparison, the average sheet resistance of the AgNWs electrode was 0.753 Ω/sq. The improvement of the conductivity for the N-MWCNTs/AgNWs composite electrode could be attributed to the addition of the N-MWCNTs (Choi 2023).

Electrochemical performance

The N-MWCNTs/AgNWs composite electrode was used to detect Cu(II) in water by SWSV. Bi(III) was added to facilitate the detection of Cu(II), as Bi(III) can form a film with Cu(II) on the surface of the N-MWCNTs/AgNWs electrode to increase the detection sensitivity (Ngoensawat et al. 2022). As shown in Fig. 3a, a significant stripping peak current was generated by the SWSV of the N-MWCNTs/AgNWs electrode in a solution containing 100 µg/L of Cu(II) (black line), while in the blank solution without any Cu(II) (red line) no peak was elicited. The result indicated that the N-MWCNTs/AgNWs composite electrode showed a high and specific voltammetric response to Cu(II). Under the same detection condition, the SWSV results of 100 µg/L Cu(II) by the AgNWs electrode, an N-MWCNTs electrode, a commercial Ag electrode and a commercial Au electrode were also recorded (Fig. 3b). The peak current of the N-MWCNTs/AgNWs electrode was approximately 70% higher than that of the AgNWs electrode and much higher than those of the N-MWCNTs, commercial Ag and commercial Au electrodes. Our laboratory showed previously that the AgNWs electrode was much sensitive than the commercial electrodes due to its nanowire structure (Sun et al. 2020; Sun and Du 2019). However, the structures of the N-MWCNTs/AgNWs electrode and the AgNWs electrode were the same and the only difference was the addition of N-MWCNTs in the composite electrode. Therefore, it was obvious that the N-MWCNTs improved the current signals from the composite electrode. These implied that coordination reaction was the main reason for the signal improvement since the nitrogen group of the N-MWCNTs caused Cu(II) to interact effectively with the N-MWCNTs/AgNWs composite electrode (Wang and Yue 2017). In addition, the 3D network of the N-MWCNTs and AgNWs allowed significantly effective charge transportation along the nanowire structure as well as sufficient and quick electrolyte diffusion to the conductor layer, which accelerated the charge transportation on the electrode surface and improved its sensitivity (Cui et al. 2014).

To verify the effect of coordination, other different carbon nanotubes were tested, such as hydroxylated multi-walled short carbon nanotubes (OH-MWCNTs-short), hydroxylated multi-walled long carbon nanotubes (OH-MWCNTs-long) and carboxylated multi-walled carbon nanotubes (COOH-MWCNTs) (Fig. 3c). Different CNTs/AgNWs electrodes with the weight ratio of MWCNTs/AgNWs at 1:10 were produced, and 100 µg/L Cu(II) solution was measured by these electrodes. The SWSV results showed that the N-MWCNTs/AgNWs electrode had the highest current among all the MWCNTs/AgNWs electrodes. This could be ascribed to the differences in the coordination because it has been reported that the complexing ability of N groups to Cu(II) was stronger than those of the COOH and OH groups (Wei et al. 2019). Thus, the experimental results of the different

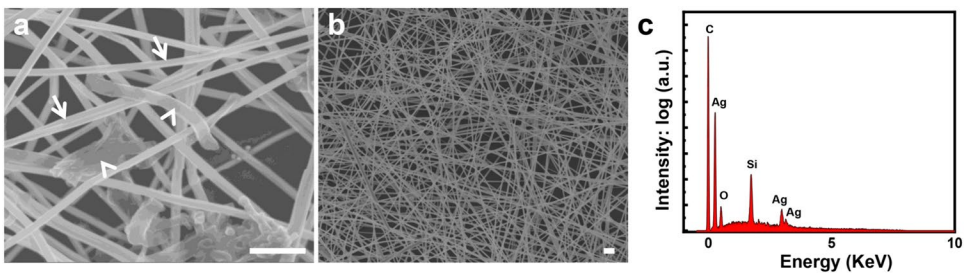

Fig. 2 SEM images of the N-MWCNTs/AgNWs nanocomposite electrode (**a**) and the AgNWs electrode (**b**). EDS analysis of the N-MWCNTs/AgNWs nanocomposite electrode (**c**). The arrows and the arrow heads in (a) indicated the AgNWs and the N-MWCNTs, respectively. Scale bars = 200 nm

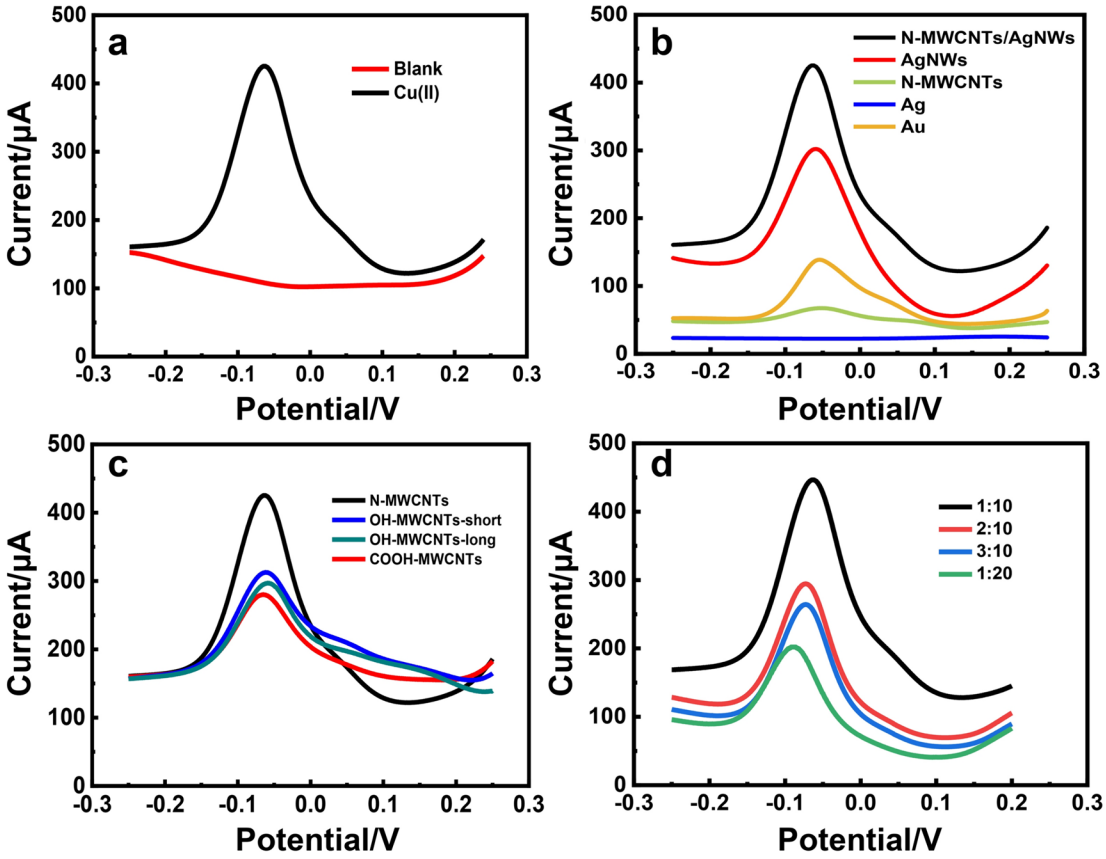

Fig. 3 **a** SWSV of the N-MWCNTs/AgNWs electrode in the absence (blank) or presence of 100 μg/L Cu(II) (Cu(II)). **b** SWSV of the N-MWCNTs/AgNWs electrode and other types of electrodes. **c** SWSV of different CNTs/AgNWs electrodes for the detection of Cu(II). **d** SWSV of the N-MWCNTs/AgNWs electrode with different ratios of N-MWCNTs to AgNWs for the detection of Cu(II). All the Cu(II) detection by the SWSV was performed in 0.1 M tartaric acid buffer solution (pH = 3.8) containing 100 μg/L of Cu(II)

MWCNTs/AgNWs electrodes confirmed our hypothesis that the addition of N-MWCNTs into AgNWs improved the sensitivity of the electrode to Cu(II) through the coordination interaction of the nitrogen group on the N-MWCNTs with Cu(II).

The ratio of N-MWCNTs to AgNWs was also an important impact factor on the electrochemical performance of the composite electrode. Four N-MWCNTs/AgNWs electrodes were prepared with the weight ratios of N-MWCNTs/AgNWs at 1:20, 1:10, 2:10 and 3:10 (Fig. 3d). The stripping peak currents suggested that the N-MWCNTs amount should be critical to the sensitivity of the electrode and the electrode with 1:10 of N-MWCNTs to AgNWs showed the highest current response. The conductivity of the AgNWs should be much higher than that of the N-MWCNTs; therefore, more amount of AgNWs had positive influence on the performance of the electrode. Furthermore, the N-MWCNTs tended to aggregate at higher concentrations that might affect the charge transportation. However, too small amount of the N-MWCNTs would impair the coordination of the electrode with Cu(II). Thus, the coordination and the ratio effects discussed above both contributed to the improved sensitivity and the faster charge transportation by the N-MWCNTs/AgNWs composite electrode (Figure S1). As a result, the N-MWCNTs/AgNWs electrode exhibited large estimated ECSA of 700 cm^2 mg^{-1}. ECSA reflects the active sites that are available for catalytic reactions. The large ECSA of the N-MWCNTs/AgNWs electrode benefited greatly from the above-mentioned complex 3D network of AgNWs and N-MWCNTs, in addition to the coordination by nitrogen doping of the MWCNTs.

Mechanical performance, repeatability and reproducibility

Compared with the traditional solid non-flexible electrodes, the novel N-MWCNTs/AgNWs electrode exhibited extraordinary flexibility, such as bendability and stretchability. It could be bent up to one hundred times and stretched up to 150% of the original length, yet retaining stable electrochemical properties. Figure 4a shows the electrochemical current variation of the N-MWCNTs/AgNWs electrode on

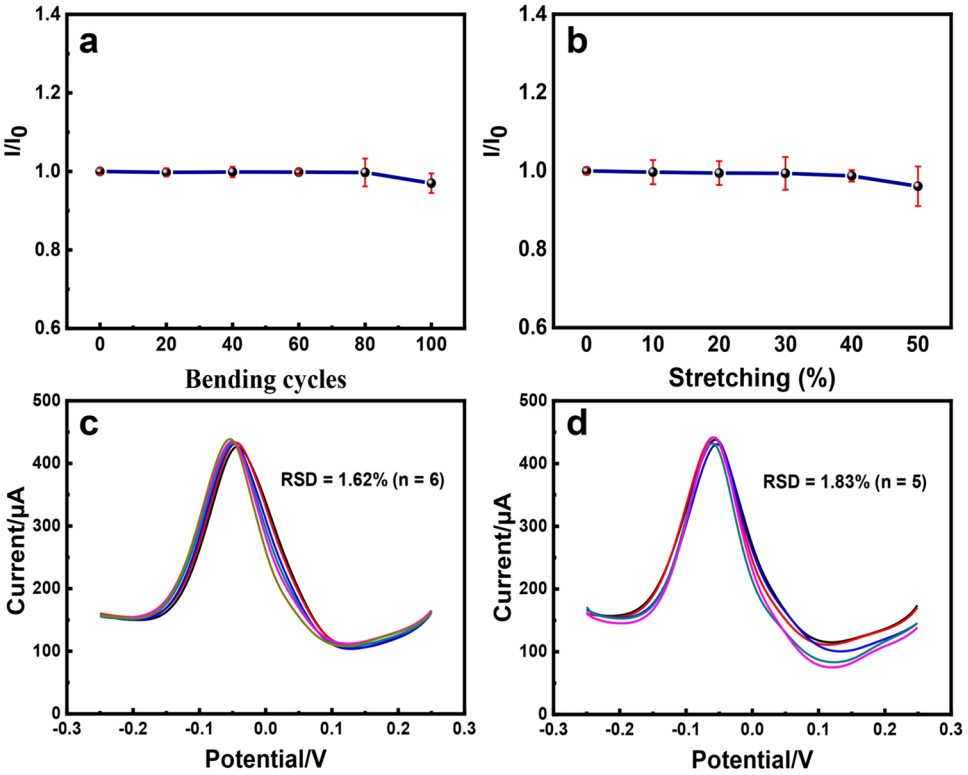

Fig. 4 **a** Peak current ratios of the N-MWCNTs/AgNWs electrode for the measurement of Cu(II) after and before bending for up to 100 cycles at 180 °. **b** Peak current ratios of the N-MWCNTs/AgNWs electrode for the measurement of Cu(II) solution after and before stretching for up to 50% strain. Repeatability (**c**) and reproducibility (**d**) of the N-MWCNTs/AgNWs composite electrode were tested in the measurement of Cu(II). All the Cu(II) measurements by the SWSV were taken in 0.1 M tartaric acid buffer solution (pH 3.8) containing 100 μg/L of Cu(II)

the measurements of Cu(II) by SWSV before and after 20, 40, 60, 80 and 100 times of 180° bending. The current variation was indicated by $I/I_{\circ}$ (ratio of the peak current after bending (I) *versus* that before bending ($I_{\circ}$)), which was slightly decreased but still at 0.9 after 100 times of bending. The electrochemical current variation of the electrode after stretching 110%, 120%, 130%, 140% and 150% was also studied by SWSV on the measurement of Cu(II), and the ratio of $I/I_{\circ}$ is compared in Fig. 4b. It was demonstrated that the electrochemical property of the N-MWCNTs/AgNWs composite electrode kept stable even after 150% of stretching. In brief, the above results proved that the composite electrode showed both favorable tensile and bending properties.

Repeatability and reproducibility are important indices to evaluate electrode performance. The same N-MWCNTs/AgNWs composite electrode was used for the successive determination of 100 μg/L Cu(II) for six times. The relative standard deviation (RSD) was 1.62% (n = 6, Fig. 4c), indicating that the N-MWCNTs/AgNWs electrode showed excellent repeatability. Five different N-MWCNTs/AgNWs composite electrodes prepared under the same conditions were used to detect the SWSV of 100 μg/L Cu(II) solution (Fig. 4d). The RSD for stripping peak current of the measurements was 1.83% (n = 5), demonstrating a good reproducibility among the electrodes.

In addition, long-term stability was tested when five N-MWCNTs/AgNWs composite electrodes were stored for 35 days and tested for the detection of Cu(II) by SWSV on different days (Figure S4). Compared with the stripping peak current on day 1, the peak currents on days 7, 14, 21, 28 and 35 remained constant with less than 1% variation, demonstrating high long-term stability of the N-MWCNTs/AgNWs composite electrodes.

Linear range and detection limit

The SWSV of different concentrations of Cu(II) solutions were determined under the optimized experimental conditions with the N-MWCNTs/AgNWs electrode. The stripping peak current of Cu(II) increased with the increase of Cu(II) concentrations (Fig. 5a). When the Cu(II) concentrations were in the range of 0.500 μg/L—100 μg/L, linear relationship was established between the concentrations of Cu(II) and the current responses of the N-MWCNTs/AgNWs electrode (Fig. 5b). The equation of linear regression was $i_p(\mu A) = 2.864C(\mu g/L) + 148.808(\mu A)$ ($R^2 = 0.9984$) and the detection limit (LOD) was 0.06 μg/L (S/N = 3). The

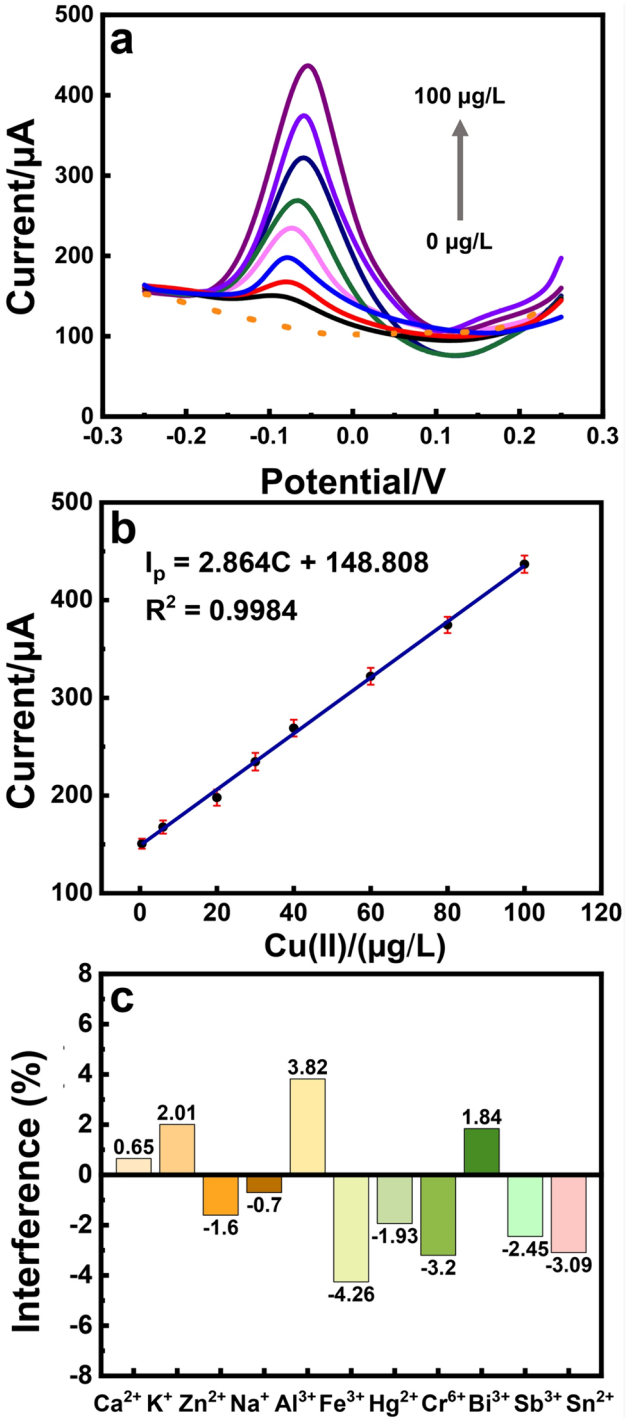

Fig. 5 **a** SWSV for different concentrations of Cu(II) (0, 0.5, 1, 10, 20, 40, 60, 80, 100 μg/L) in 0.1 mol/L tartarate–sodium tartarate buffer solution (pH = 3.8). **b** Linear 20 fitting curve of Cu(II) concentrations and stripping peak currents. Error bars = SD (n = 3). **c** SWSV peak current variations (% interference) of the N-MWCNTs/AgNWs composite electrode for the measurements of 100 μg/L Cu(II) in the presence of 1000 μg/L of Ca(II), K(I), Zn(II), Na(I), Al(III), Fe(III), Hg(II), Cr(VI), Bi(III), Sb(III) and Sn(II), respectively

detection performance of the method was compared with other methods shown in Table 1, which showed that the detection range of the method was wider and the detection limit was lower than those in most publications were.

The influence of interfering metal ions on the detection of Cu(II) was investigated (Fig. 5c). The SWSV peak current of Cu(II) was measured by adding 1000 μg/L of Ca(II), K(I), Zn(II), Na(I), Al(III), Fe(III), Hg(II), Cr(VI), Bi(III), Sb(III) and Sn(II), in 100 μg/L Cu(II) solution, respectively. The Cu(II) was determined by SWSV, and the relative errors (n = 5) were all less than 5.0%. Therefore, the interference ions had little influence on the Cu(II) peak current, indicating that the N-MWCNTs/AgNWs composite electrode had strong anti-interference ability.

Determination of Cu(II) in actual water samples

Cu(II) contents in the tap and lake water samples were determined with the composite electrode by the method developed in this study and by ICP–MS (Table 2). As summarized in Table 2, the comparative results between our and the ICP–MS methods suggest that the flexible N-MWCNTs/AgNWs composite electrode is suitable for analysis of trace Cu(II) in real samples. Among them, the tap water met the Hygiene Standard for Water Used in Daily Life (GB5749-2006), and the river and lake located on the campus of the Dalian University met the class III Environmental Quality Standards for Surface Water (GB3838-2002) (Lin et al. 2021).

Conclusions

In this study, a new flexible N-MWCNTs/AgNWs electrode was developed with high electrical conductivity, owing to the addition of N-MWCNTs into the AgNWs. The controlled addition of N-MWCNTs into the AgNWs also resulted in improved electrolyte penetration, adsorption and coordination reaction. The flexible N-MWCNTs/AgNWs electrode exhibited an excellent performance in Cu(II) detection in terms of limit of detection, linear range, flexibility, anti-interference, repeatability and reproducibility. Moreover, the electrode has successfully been utilized for detecting Cu(II) in real natural water samples. Due to its excellent performance and flexibility, this PDMS-based flexible composite electrode may aid in the future development of novel environmental monitoring and wearable devices.

Table 1 Comparison of the detection limit and linear range for Cu(II) determination

Electrochemical Platform	Method	Linearity range (μg/L)	Detection limit (μg/L)	References
SGAuNP-CE	ISE	$27.5–6.4\times10^4$	25.6	Mashhadizadeh and Talemi (2011)
MWCNTs-GC	DPV	32–79	4.8	Dalmasso et al. (2015)
GO/MWCNT-ITO	SWASV	3.2–158.9	0.76	Guo (2015)
GCE/GO/Fe3O4@PMDA/AuNPs	SWASV	0.5–750	0.11	Nodehi et al. (2021)
Gold nanostar-modified electrode	SWASV	0–250	42.5	Sullivan et al. (2020)
Nanocrystalline boron-doped diamond electrode	DPASV	7.7–100	40	El Tall et al. (2007)
N-MWCNTs/AgNWs	SWSV	0.500–100	0.06	This work

Table 2 Detection of Cu(II) in actual environmental water samples

Sample	Original (μg/L)	Added (μg/L)	Found (μg/L)[a]	Recovery (%)[a]	Found by ICP–MS[a]
Tap water 1	3.7	0.5	4.24 ± 0.07	101.0 ± 1.67	4.21 ± 0.02
Tap water 2	3.4	5	8.39 ± 0.08	99.8 ± 0.90	8.43 ± 0.02
Later water 1	50.5	0.5	50.87 ± 0.45	99.7 ± 0.90	51.13 ± 0.21
Lake water 2	50.2	5	55.80 ± 0.56	101.1 ± 1.00	55.7 ± 0.26

[a] Mean ± Standard deviation; n = 3

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Declarations

Conflict of interest The authors declare no conflict of interest.

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