Electrochemistry Behaviors of Cu at Embedded Carbon Nanotubes Modified Bismuth-Film Electrode

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Abstract. The embedded carbon nanotubes modified bismuth-film electrode was prepared and the electrochemical behaviors of Cu at the modified electrode was studied with cyclic voltammetry in this work. The result shows that the oxidation peak of Cu at the modified electrode is single and irreversible. The oxidation peak potential ($E_{pa}$) and current ($i_{pa}$) are 0.045V and 10.90$\mu$A, respectively, with two protons and electrons transfer in this process. Then, the optimum condition of copper differential potentiometric stripping are the -1.1 V of accumulation potential, 0.4mg/L of bismuth concentrations, and pH 4.6 in the HAc-NaAc buffers. The height of peak is linear with the mass concentration of Cu over the range from 0 to 50.0$\mu$g/L under the best conditions.

1. Introduction
The element of copper is needed to crops grown [1], one of the necessary mimim elements of human, and also one of the important elements of heavy metal pollution in soil [1]. Deficient copper of plants can affect protein synthesis, and inhibit the photosynthesis capability, which led to reduce production. It also can influence the growth of pollen and ovule. [2] The deficiency of Cu can cause anemia and easy to infertility to the human. As above, it will cause copper poisoning of plants when the copper content in soil is over a critical concentration. The traditional voltammetric analysis of heavy metals has the potential danger to the environment and analysts for using mercury film electrode. In this paper, a novel modification electrode with embedded carbon nanotubes and bismuth composite membrane was developed based on our research on bismuth film electrode. This electrode improved the combination of electrode and carbon nanotubes with the method of inlaid modified modification of carbon nanotubes, and enhanced the sensitivity and stability of method by the catalysis effect of carbon nanotubes.

2. Experiments
2.1. Experimental apparatus, material, reagent
Instrument: MEC-12B type multifunction electrochemical analysis system (Jiangsu jiang distribution analysis instrument Co., LTD); MP-2 stripping analyzer; MCP-2T polarographic workbench (Shandong telecom seven factory); three electrode system: work electrode-embedded carbon nanotubes modified bismuth-film electrode, reference electrode - saturated calomel electrode (SCE), compare electrode-Pt electrode.
Cu-standard solution: 0.10 g·L⁻¹; 
Buffer solution: 0.10 mol·L⁻¹ HAc- 0.10 mol·L⁻¹ NaAc (pH = 4); concentrated nitric acid; perchloric acid.
Sample: tailings (collected from Gejiu City, Yunnan Province)

2.2. Experimental

2.2.1. Embedded carbon nanotubes modified bismuth-film electrode preparation. First, put multi-walled carbon nanotubes (MWNT) into the concentrated hydrochloric acid ultrasound [3] for 7.5 h in order to carry on the passivation. Then, the ultrasound-well MWNT was washed with ultrapure water to neutral after refluxed in concentrated nitric acid at 140 °C for 8 h. In the end, the sample was grinded into fine powder after dried at 100 °C. As the reported by Qing Cao [4], -OH and -COOH were introduced when the MWNT, treated with concentrated nitric acid, opened the port. With the mechanical grinding method, as follows: the glassy carbon electrode was initially polished into a mirror with a polishing powder of 0.05 µm Al₂O₃, then ultrasonic cleaned 10 min in 1:1 nitrate acid, 1:1 ethanol, and ultrapure water, respectively. Next, take a piece of light vegetable parchment, and then put approximately 0.5 g multi-walled carbon nanotube powder in it. Finally, glassy carbon electrode was grinded carefully in above vegetable parchment for a period of time till appear a layer of dense black film, that is the embedded carbon nanotubes modified electrode. Put the grinded-well carbon nanotube in the among 1 mol·L⁻¹KNO₃, 1% HNO₃, and 5×10⁻⁴ mol·L⁻¹ bismuth stirring sink effusion[6], set the bismuth deposition potential as -0.5 V and deposition time as 300 s, then got a layer of black uniform bismuth film in the electrode surface. Add 20 μL 0.20 g·L⁻¹ solution of Bi(NO₃)₃·5H₂O into situ-plate bismuth film each time before the determination of differential potentiometric stripping analysis and Bi will participate in electrode determination, which deposits on the electrode surface with the progressing of electrode accumulation and stripping.

2.2.2. The electrochemical behaviors of Cu on the cyclic voltammetry. A certain amount of Cu standard solution, which taken with a pipette, was diluted to 10 mL using pH=5.4, 0.2 mol·L⁻¹ buffer solution of HAc-NaAc, shaked well, and then analyse the behaviors of Pt as the scanning speed of 0.10 V/s and record cycle volt-ampere curve (CV) within the potential range of -0.3~0.7V with three electrode system.

2.2.3. The determination of the Cu differential potentiometric stripping. Transfer 2.5 mL buffer solution of HAc-NaAc, concentration of 0.20 mol·L⁻¹, to a 10-mL volumetric flask, dilute to volume, and mix well, transfer to the electrolytic cup. Then add 10 μL and 20 μL solution of 0.10 g·L⁻¹ Cu standard and Bi, respectively, to it by micro-injector. Insert the three electrode system to above solution, adjust the maximum potential -0.30 V, upper potential 0.10 V, accumulation potential -1.00 V, clean potential 0.30 V, and enter the appropriate time of static, accumulation, clean, and sensitivity etc. Next, start the program controller, auto-complete the electrolysis, accumulation and dissolution by instrument, measure the dissolution curve of dt/dE vs. E, record the stripping peak height at the -0.02 V. Add 10.0 μL of 0.10 g·L⁻¹ Cu standard solution to un-test solution by micro-injector, test the peak height after adding standard and simultaneously determine the reagent blank, calculate the Cu content by the standard addition method.

2.2.4. The sample pretreatment and determination. The soil sample pretreatment: dry the collected soil sample and smash to around 100 mesh. Weigh about 2.00 g sample in 100 mL of porcelain crucible, put into the muffle furnace and calcine at 120 °C for 1h, then at 500 °C for 5 h till ashing completely. Add 10 mL concentrated HNO₃ into the cooled sample, nitrify entirely on electric hot plate, then add 2 mL HF to nitrify almost colorless, mix with some water and adjust pH to 4.6 with the solution of NaAc, then transfer to 25-mL volumetric flask, dilute to volume, and do the blank test. Sample determination: take 5 mL disposed-well solution of soil sample in 10-mL volumetric flask,
dilute with pH 4.6 buffer solution of HAc-NaAc to volume, then transfer to electrolytic cup and add 20 μL solution of 0.20 g·L⁻¹ Bi³⁺ by micro-injector. The dissolution of peak height of trace copper was measured using “2.2.3” method, and calculate the Cu content by the standard addition method.

3. Results and discussion

3.1. Usage results of embedded carbon nanotubes electrode
The signals of blank line peak and cyclic voltammetry related to Cu are all stronger than bare glass carbon electrode after using embedded carbon nanotubes modified glass carbon electrode as working electrode. There are no new re-dox peaks within the scope of the electrochemical window, indicating that there are no interference peaks in the studied bound so the electrochemical analysis can be performed. From the Fig. 1, it can be seen that the sensitivity of embedded carbon nanotubes electrode is higher than bare glass carbon electrode, exhibits more sharp-angled peaks, and more obvious signal of peak current after adding Cu into the buffer solution of pH=4.6 HAc-NaAc. The higher sensitivity indicates that the multi-walled carbon nanotubes has been embedded into the electrode. Meanwhile the peak of Cu exhibits satisfactory precision, and the RSD of the oxidation peak height is 2.4 % (n=10) after continuously testing over 10 times.

To sum up, the present study indicates that the stability, reproducibility, and sensitivity of the embedded carbon nanotubes modified glass carbon electrode are all significantly better than bare glass carbon electrode, and it is suitable for the determination of trace Cu.

3.2. The effects of pH and the determination of electron transfer number
The cyclic voltammetry behaviors of 0.03g/L Cu in the buffer solution of HAc-NaAc at different pH of 3.6, 4.2, 4.6, 5.0, 5.4, 5.6, 5.8, 6.0, within the potential range of -0.3~0.7V, and at the scan speed 0.11 V/s, as shown in Fig 5. The Table 2 shows the peak current and peak potential value of Cu in the buffer solution of HAc-NaAc at different pH. As seen in Fig 5 and Table 2, the peak current value is largest when the pH of HAc-NaAc at 4.2 to 4.6. Any value outside this range will cause the value small. It could be due to hydrolysis of partial cadmium, reduce the peak current, with decreasing acid concentration. However, precision becomes lower, against the determination of peak current, with increasing acid concentration. So we chose the
buffer solution of HAc-NaAc at pH of 4.6 as the determination medium of cyclic voltammetry in this work.

![Graph showing the effect of pH on peak current](image)

**Fig 2. The effects of pH on the peak current of Cu**

The Cu is irreversible system, so the peak current (Ip) and adsorption charge (Q) meet relationship according to the Laviron theory:

\[
i_p = \frac{n^2 F^2 A T v}{4 R T} = \frac{n F Q v}{4 R T}
\]

Based on this equation, n, the number of electrons of electrode reaction, can be calculated. In the equation, adsorption charge Q, Q = nFAT, is the peak area of cyclic voltammograms in single process, F is the constants of Faraday, A is adsorption quantity, R is the molar gas constant, T is absolute temperature which based on 273K. According to the above conditions, the electron transfer no. is 2.

3.3. The determination of the differential potentiometric stripping of Cu

3.3.1. The effects of pH on the RSD value and peak height. The pH value has a big impact on the determination of sensitivity and precision in the determination of differential potentiometric stripping. The shape-well peak of digestion can be gained in a weak acid medium. The effect of pH on relative standard deviation and the differential potential stripping peak height was shown in Fig 3. It can be seen that the precision becomes worse, peak height is lower, and the sensitivity is reduced no matter high or low pH. The reason is that the overpotential of hydrogen on the bismuth is low, resulting hydrogen evolution. The stronger hydrolysis of Bi^{3+} is easy to hydrolyze in the high-pH condition. It is beneficial for the determination of Cu because the Cu exhibits the biggest peak, lowest RSD, and good precision at the 4.4 to 5.4 pH value. The peak height and peak current reach the maximum value at 4.4 pH. So we chose the buffer solution of HAc-NaAc at pH of 4.4 as the determination medium of Cu in this work.
3.3.2. The effect of coating membrane method. The coating membrane method exists pre-coating membrane method and chronoamperometry coating membrane method. The latter was chose in this experiment. Mix up the Bi-solution with the Cu being tested, then the alloy, was formed by electrolysis of Cu and Bi simultaneously, deposits at the embedded carbon nanotube glassy carbon electrode. So that the coating of Bi-film is to keep fresh and the repeatability of determination. To the pre-coating membrane method, coat the Bi on the surface of electrode in advance, the Bi-film will be gradually lost during use and relatively damaged, is difficult to guarantee the repeatability of determination. So we chose the chronoamperometry coating membrane method.

3.3.3. The stripping peak of Cu at embedded carbon nanotube glassy carbon electrode. Determine the dissolution behaviors of 3.0 μg Cu at embedded carbon nanotube glassy carbon electrode under the conditions which contains the 4.4 of pH, 0.4 g·L⁻¹ of Bi concentration and -1.00 V of accumulation potential, and compared to un-embedded electrode, the results are shown in figure 4. As can be seen from the Fig4, the Cu exhibits well dissolution behaviors on the differential potentiometric stripping behavior. There is a obvious peak on the embedded carbon nanotube glassy carbon electrode, significantly higher than the un-embedded electrode, 224.02 and 29.57 height respectively, but the potential range changes are not very noticeable. These instruct that it can obviously increase the sensitivity using the embedded carbon nanotube glassy carbon electrode as working electrode.

3.3.4. The linear range and detection limit. In this work, the concentration of Cu is 0~50.0 μg·L⁻¹ under the optimum determination conditions and set instrumental sensitivity S as 100, electrolysis time...
as 180s, and solution volume as 10 mL. The equation of linear regression as: $y = 973.91x - 13.422$ ($r = 0.9952$). In this experiment, we took the electrolytic accumulation time 120s, the content of Cu 1.5 $\mu$g·L$^{-1}$ with the buffer solution of HAc-NaAc, pH 4.6 and 0.20mol·L$^{-1}$, repeated 12 times during that time, then rejected the data of 1 and 2 to calculate the standard deviation, the detection limit of Cu equals to divide the content of Cu by peak, then Multiply by 3 times of the standard deviation, during the 120s of the accumulation time, obtained that lowest detective density of Cu was 0.90 $\mu$g·L$^{-1}$.

3.3.5. The determined results of the sample. The near mine soil samples got from Datun Gejiu City, Honghe Prefecture were determined in this study that set instrumental sensitivity S as 50, electrolysis time as 50s, cleaning time as 30s, and solution volume as 10 mL, the results as shown in Table 3. It can be seen that the content of Cu is high in this area, to a maximum of 8.5510 mg·kg$^{-1}$, 1.34% ~ 6.60 % of RSD, and 95.3%~112.0 % of recovery, so we conclude that the area is polluted seriously by copper and should be received sufficient attention.

### Table 1. The analysis results of Cu in soil samples

| Sample | Cu content (mg·kg$^{-1}$) | RSD (%) | adding standard (mg·kg$^{-1}$) | measured value (mg·kg$^{-1}$) | recovery rate (%) |
|--------|--------------------------|---------|-------------------------------|-------------------------------|-------------------|
| 1      | 0.4028                   | 3.79    | 0.50                          | 0.9396                        | 107.4             |
| 2      | 4.8170                   | 6.60    | 4.00                          | 9.2980                        | 112.0             |
| 3      | 2.9550                   | 2.45    | 2.00                          | 4.8680                        | 95.7              |
| 4      | 7.2191                   | 4.70    | 5.00                          | 11.9841                       | 95.3              |
| 5      | 8.5510                   | 7.32    | 5.00                          | 13.6700                       | 102.4             |
| 6      | 7.8284                   | 1.34    | 5.00                          | 12.6497                       | 96.4              |

4. Conclusion

The cyclic voltammetric behavior and differential potentiometric stripping behavior of Cu were determined using embedded carbon nanotube modified electrode as Woking electrode in this paper. The results show that the adsorption process of Cu at the embedded carbon nanotube electrode is controlled by adsorption diffusion in the 0.1 mol·L$^{-1}$ pH = 4.6 buffer solution of HAc- NaAc, and appear a obvious oxidation peak within the potential range of -0.10 ~0 V. Meanwhile the differential potentiometric stripping peak of Cu is well and the sensitivity is better than bare glass carbon electrode. The reproducibility and precision of the method are good, and environmentally friendly that using Bi instead of toxin-Hg.

Acknowledgments

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