# Supplementary information

## Low-cost bimetallic FeNi alloy nanoparticles loaded on nitrogen-doped carbon nanotubes for electrochemical sensing of copper ions

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## Experimental section

### Materials and reagent

N-CNTs (multi-walled carbon nanotubes, 95%) were provided by Chengdu Organic Chemicals Co., Ltd. $Ni(NO_3)_2{\bullet}6H_2O$, $Fe(NO_3)_2{\bullet}9H_2O$, and $Cu(NO_3)_2{\bullet}3H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd., which is located in Shanghai, China. All the chemical reagents involved in the experiments are of analytical grade or better and were used as received. 0.1 M HAc-NaAc, prepared by mixing different proportions of HAc and NaAc, was used as the supporting electrolyte. All aqueous solutions are prepared using ultrapure water (Milli-Q, Millipore), with resistivity higher than 18.2 MΩ·cm.

### Apparatus

Transmission electron microscope (TEM) images were obtained on a JEOL 2100F transmission electron microscope with a 200 kV accelerating voltage. X-ray diffraction (XRD) patterns were carried out with a D8 advance diffractometer with a Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS) measurements were performed with an Ultra Axis spectrophotometer equipped with a monochromatic Al Kα source operated at 150W. Electrochemical experiments were carried out on a CHI 660 E electrochemical workstation with a conventional three-electrode system. A bare or modified glassy carbon electrode (GCE, 3 mm in diameter), a Pt wire, and an Ag/AgCl (saturated KCl) were used as working electrode, counter electrode and reference electrode, respectively. All electrochemical measurements were carried out at room temperature.

### Parameters optimization for electrochemical determination of $Cu^{2+}$

To achieve the maximum efficiency of FeNi/N-CNTs/GCE for the electrochemical determination of $Cu^{2+}$, it is necessary to optimize the detection conditions (e.g., the raw material ratio, the pH of the buffer, the amount of the modifier, the deposition time, and deposition potential) prior to quantitative analysis.

The molar ratio of the two metallic nitrates was first optimized and controlled at 1:3, 1:1, 3:1, and 7:3 (Fe: Ni), respectively. The obtained cyclic voltammogram (CV) is shown in Figure S1. As can be seen, the highest response current of $Cu^{2+}$ is achieved at a molar ratio of Fe: Ni = 1:3. Consequently, this molar ratio was adopted for the preparation of FeNi/N-CNTs nanocomposites.

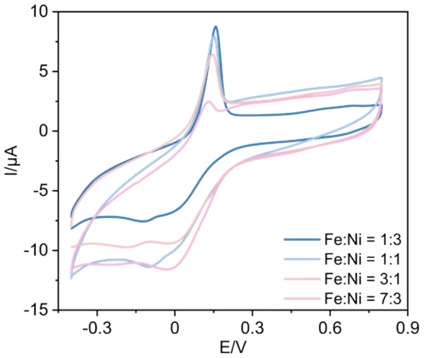

**Figure S1.** CV curves of FeNi/N-CNTs/GCE in pH 4.0 HAc-NaAc buffer containing 400 μM $Cu^{2+}$ with different mass ratio of Fe and Ni.

The concentration of FeNi/N-CNTs dispersion coated on the electrode surface significantly influences the performance of the sensor. Figure S2a shows the CV curve of GCEs modified with different concentration of FeNi/N-CNTs dispersion for the determination of 400 μM $Cu^{2+}$. As illustrated, the response current of $Cu^{2+}$ increases as the concentration rises from 0.5 to 1.0 mg $mL^{-1}$, which is related to the increased active sites. When the concentration is further increased to 1.5 mg $mL^{-1}$, the response current tends to decrease. This is because excessive loading of FeNi/N-CNTs dispersion on electrode surface hinders the electron transfer. Hence, 1.0 mg $mL^{-1}$ of FeNi/N-CNTs dispersion was selected as the optimal concentration for electrode modification. Subsequently, the effect of the volume of FeNi/N-CNTs dispersion on the response current of 200 μM $Cu^{2+}$ was investigated with volume of 1 μL, 3 μL, 5 μL, 7 μL, and 9 μL, respectively. The results in Figure S2b show that when the volume of FeNi/N-CNTs is less than 5 μL, the response current gradually increases, while when the volume exceeds 5 μL, the response current actually decreases. So, 5 μL of 1.0 mg $mL^{-1}$ FeNi/N-CNTs dispersion was finally coated on the GCE surface to obtain the modified electrodes.

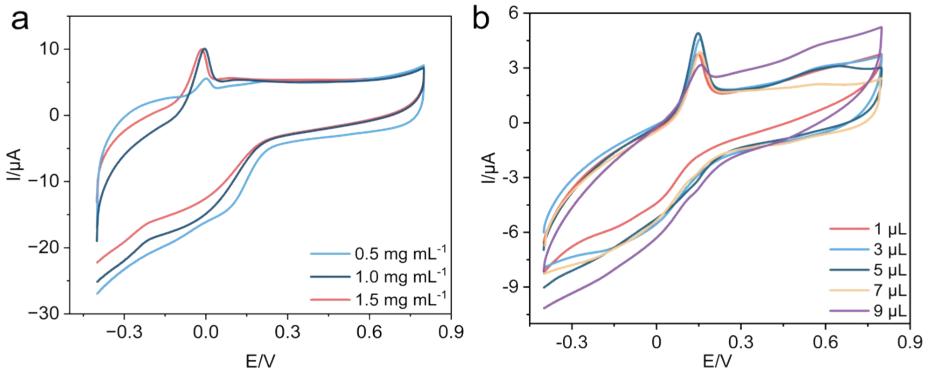

**Figure S2.** CV curves of FeNi/N-CNTs/GCE in pH 4.0 HAc-NaAc buffer containing 400 μM

$Cu^{2+}$ with different concentration of FeNi/N-CNTs dispersion (a), CV curves of FeNi/N-CNTs/GCE in pH 4.0 HAc-NaAc buffer containing 200 μM $Cu^{2+}$ with different volume of FeNi/N-CNTs dispersion (b).

Usually, HAc-NaAc buffer is more conducive to the detection of heavy metal ions. Therefore, in this study, a series of HAc-NaAc buffers with different pH values were prepared and investigated. Figure S3 presents the relationship between the pH values and the response current of $Cu^{2+}$. It is evident that the response current of $Cu^{2+}$ initially increased as the pH increased and reached its maximum at pH 4.0. After that, the response current decreased with further increasing pH. This phenomenon can be ascribed to the hydrolysis of $Cu^{2+}$, resulting in the generation of insoluble $Cu(OH)^+$ or $Cu(OH)_2$ species. This reduces the availability of free $Cu^{2+}$ for effective electrochemical interactions [1]. The lower response under acidic conditions ($pH < 4.0$) can be attributed to proton competition for the Lewis base sites (pyridinic N or $M–N_x–C$), which hinders the coordination of $Cu^{2+}$. This pH dependence is characteristic of a Lewis acid–base interaction. Therefore, a pH 4.0 HAc-NaAc buffer was selected as the optimal supporting electrolyte for the electrochemical tests.

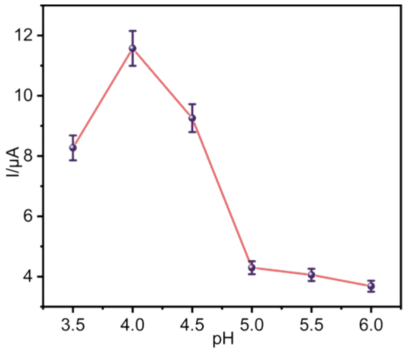

**Figure S3.** Effect of pH on the oxidation peak current of $Cu^{2+}$.

One of the crucial parameters for stripping analysis is deposition potential and deposition time, which play a crucial role in enhancing the adsorption of heavy metal ions onto the electrode surface, thereby improving the sensitivity. The effect of deposition potential and deposition time on the response current of $Cu^{2+}$ was investigated (Figure S4). Figure S4a depicts the variation of response current of $Cu^{2+}$ with the deposition time from 0 to 180 s. As can be seen, the response current of $Cu^{2+}$ almost linearly increases from 0 to 150 s. When the deposition time exceeds 150 s, the increase in current becomes smaller. Considering both sensitivity and analysis speed, a deposition time of 150 s was selected as the optimal value. The influence of deposition potential on the response current was investigated over the range of 0 to -1.6 V (vs. Ag/AgCl) with a fixed deposition time of 150 s

(Fig. S4b). The response current increased rapidly as the deposition potential shifted from 0 to -1.4 V, indicating enhanced reduction and accumulation of $Cu^{2+}$. However, when the deposition potential became more negative than -1.4 V, the response current decreased. This decrease is primarily attributed to the hydrogen evolution reaction (HER), which competes with $Cu^{2+}$ reduction and may generate gas bubbles that partially block the electrode surface [2]. Although hydrogen evolution at -1.4 V cannot be completely ruled out, the maximum response current observed at this potential suggests that the beneficial effect of enhanced $Cu^{2+}$ reduction outweighs the adverse effects of HER under our experimental conditions. To balance sensitivity and electrode stability, -1.4 V was selected as the optimal deposition potential.

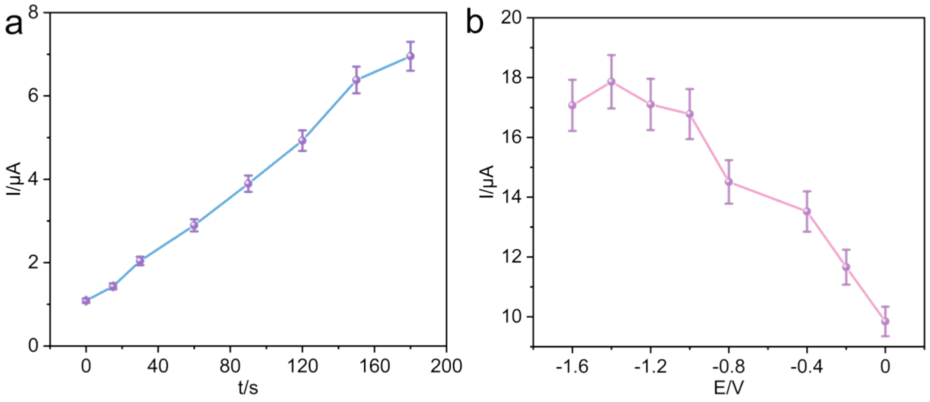

**Figure S4.** Effect of deposition time (a) and deposition potential (b) on the oxidation peak current of $Cu^{2+}$.

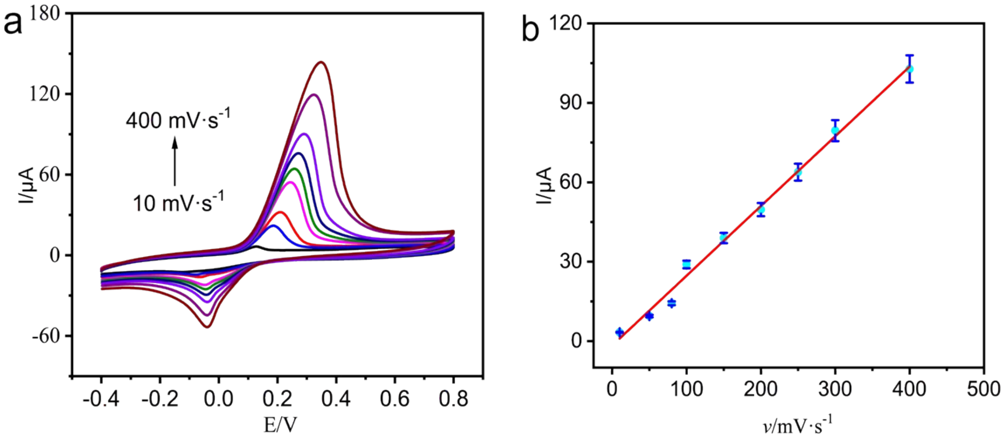

**Figure S5.** CV curves of FeNi/N-CNTs/GCE in 0.1 M HAc-NaAc buffer (pH 4.0) containing 400 μM $Cu^{2+}$ at different scan rates (10–400 mV $s^{-1}$) (a) and the corresponding plots of anodic peak current ($I_{pa}$) vs. scan rate ($v$) (b).

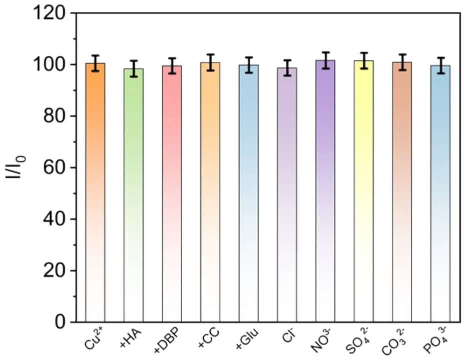

**Figure S6.** Interference study of FeNi/N-CNTs/GCE toward 1 μM $Cu^{2+}$ solution with 100 μM of various inorganic anions and organic interferents.

## References

[1] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations. Wiley, 1976.

[2] J. Wang, Stripping Analysis: Principles, Instrumentation, and Applications. VCH Publishers, 1985.