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A Simple and Facile Electrochemical Sensor for Sensitive Detection of Histidine Based on Three-Dimensional Porous Ni Foam

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The commercially available three-dimensional porous Ni foam was presented as a novel electrochemical sensing platform for sensitive detection of histidine (His). Ni foam exhibited excellent electrocatalytic activity towards the oxidation of histidine. Based on the low cost Ni foam, a simple and sensitive His sensor was developed, with the linear range from 0.15 to 20.3 μM (R^2=0.9978) and the detection limit of 50 nM in a 0.1 M NaOH solution. The proposed method was also successfully demonstrated for the detection of histidine in human urine sample.

Keywords: Ni foam, electrochemical sensing, histidine, electrocatalytic activity

1. INTRODUCTION

Histidine (2-amino-3-(4-imidazolyl)-propanoic acid, His), a neurotransmitter or neuromodulator, is an essential constituent of proteins. It plays a vital role in biological systems. For instance, His control the transport of metal in biologically bases [1] and minimize internal bleeding from microtrauma [2]. However, it was found that excessive His could result in symptoms of intoxication [3], causing stress and psychological disorders, such as anxiety, schizophrenia and thrombotic disorders [4]. In addition, the persistent deficiency of His was reported to be associated with rheumatoid arthritis, nerve deafness, liver cirrhosis, and so on [5]. Therefore, simple, accurate,

and sensitive detection of His is very important for biological applications including both research and clinical treatment.

Up to date, a number of analytical techniques have been reported in the development of His detection, including chromatography [6-8], fluorescence [9, 10], mass-spectrometry [11], capillary electrophoresis [12, 13], colometry [14-17], resonance light scattering [18], and atomic spectrometry [19]. These methods still suffer drawbacks, such as tedious analysis processes, long analysis time, and expensive instrument. Among other analytical methods, electrochemical method is gaining more and more attention among for the detection of His because of its simplicity, low cost, high sensitivity and fast analysis. However, the electro-oxidation of His at traditional electrodes requires high overpotential. Various electrocatalysts have been used to decrease the overpotential of His including Nickel hydroxide nanocrystals [20], carbon nanotubes-Cu_2O [21], bimetallic nickel-iron-carbon nanotubes [22], Fe(III)-porphyrin [23], $Ni(OH)_2$ hourglass-like nanostructures [24], and carbon nanotubes-copper microparticles [25]. These electrocatalysts materials are expensive or need tedious synthesis processes. In the work, low cost and commercially available three-dimensional porous Ni foam was employed as a novel electrocatalyst for the sensitive detection of histidine (His), and satisfied results were obtained.

2. EXPERIMENTAL

2.1. Chemicals and solutions

His, ascorbic acid (AA), L-reduced glutathione (GSH), uric acid (UA), and glucose were purchased from Sigma-Aldrich. Ni foam was acquired from Nanjing XFNano Materials Tech Co., Ltd. All other chemicals were of analytical reagent grade, and doubly distilled water was employed to prepare all the solutions. 0.1 M NaOH solution was used as the background electrolyte.

2.2. Apparatus

Scanning electron microscopy (SEM) images were obtained with a Hitachi SU8010 (Japan) scanning electron microscope. A CHI 660E electrochemical workstation ((Shanghai CH Instruments, China) was used to perform all the cyclic cyclic voltamograms (CVs) and i-t curves experiments with a conventional three-electrode system, which included a Ni foam (1 cm ×1 cm) as the working electrode, an Ag/AgCl (saturated KCl) as the reference electrode , and a platinum coil as an auxiliary electrode. For the CVs experiments, the scan rate was set to 0.1 V/s from 0 to 0.7 V. In case of i-t curves experiments, the applied potential was 0.57 V.

3. RESULTS AND DISCUSSION

The electrode surface morphology of Ni foam was characterized by SEM. Fig. 1 depicts the SEM images of Ni foam electrode. Ni foam presents three-dimensional porous structure, which can provide large electroactive surface. Fig.2 is the typical CVs obtained at a Ni foam electrode in the

absence (dotted line) and presence (solid line) of 5 mM His in 0.1 M NaOH at a scan rate of 0.1 V/s. A pair of redox peaks appeared at the Ni foam electrode (A, dotted line) at the potential of about 0.53 and 0.37 V, respectively, which was ascribed to the electrochemical transformation between $Ni(OH)_2$ and NiOOH according to the following reaction [26].

$$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^- \quad (1)$$

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \quad (2)$$

When His was added into the solution, the oxidation current increased and the oxidation peak appeared at 0.57 V.

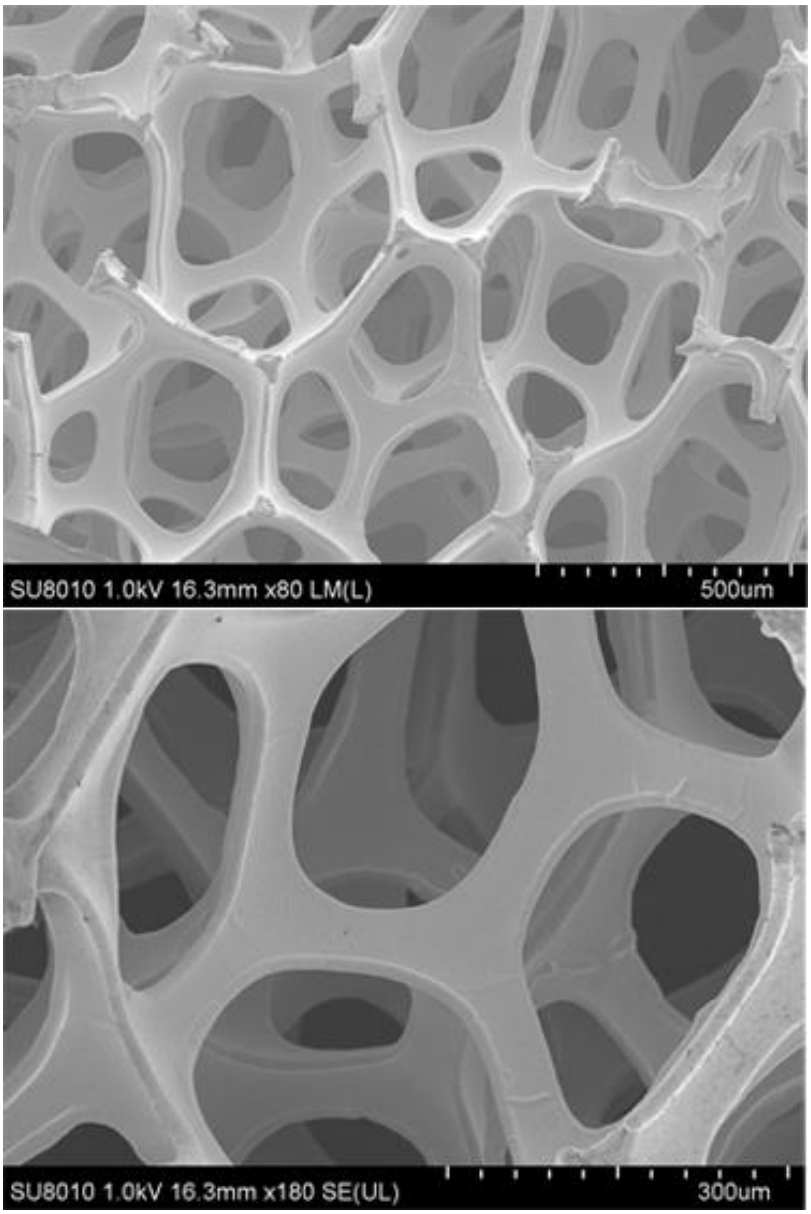

Figure 1. Scanning electron microscopy (SEM) image of Ni foam.

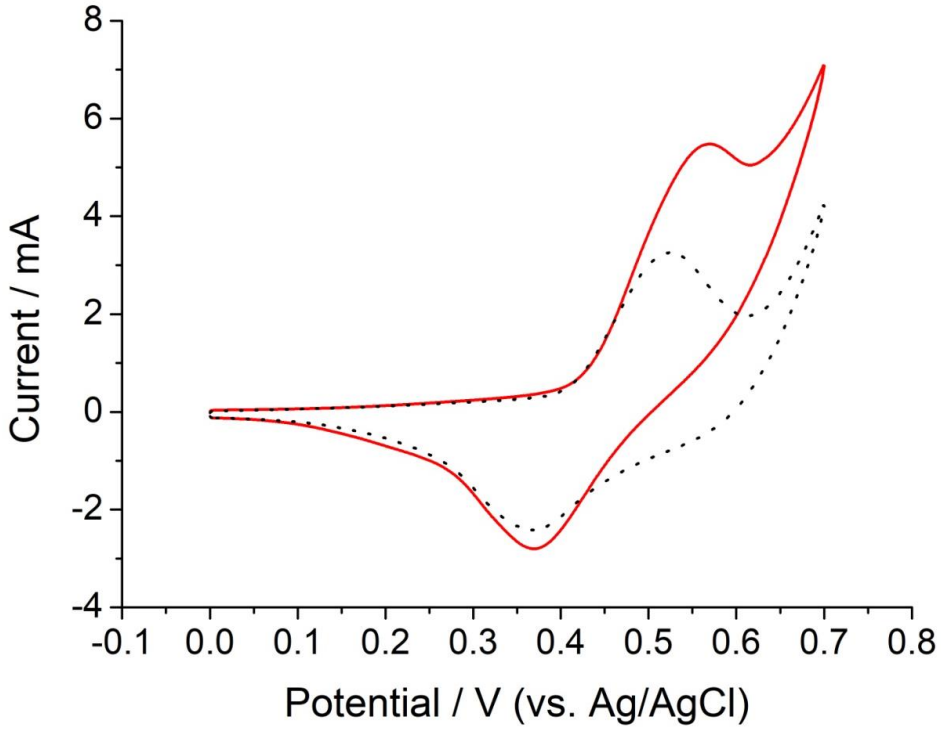

Figure 2. Typical CVs acquired at a Ni foam electrode in the absence (dotted line) and presence (solid line) of 5 mM His in 0.1 M NaOH at a scan rate of 0.1 V/s.

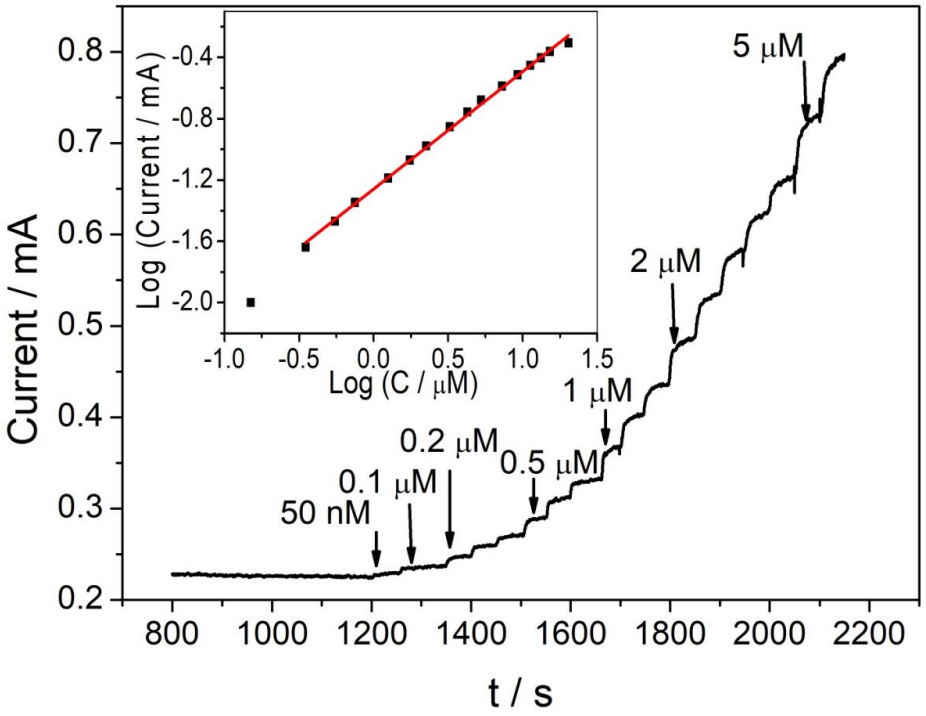

Figure 3. Amperometric response of the Ni foam electrode to the successive addition of His in stirred 1.0 M NaOH at an applied potential of 0.57 V. *Insets*: calibration curve for the steady-state current upon the addition of different His concentrations.

This suggested that Ni foam exhibited an excellent electrocatalytic activity for the oxidation of His. Next, Ni foam electrode was applied for the ameperometric detection of His in stirred 1.0 M NaOH at an applied potential of 0.57 V, as shown in Fig. 3. As can be seen, Ni foam elctrode had a fast and sensitive response to the successive injection of His. The calibration curve shows that the amperometric current of the sensor presents a linear dependence on His concentration over the range from 0.15 μM to 20.3 μM (I/μA=0.766C/μM-1.26, R^2=0.9978) with a detection limit of 50 nM. A comparison of the analytical parameters for the determination of His by our proposed method and other reported methods were summarized, as shown in Table 1.

Table 1. Comparison of the present method with reported methods for the analysis of His

Method	Linear range	Detection limits	Literature
NPs-based UV–visible spectroscopy	0.001-100 μM	4.2 nM	[27]
Cyclic voltammetry	0.1 μM-0.5 mM	80 nM	[28]
Fluorescent probe	0.5-100 μM	76 nM	[29]
CZE–AD	~	0.043 μM	[21]
Colorimetric and visual determination	~ -3.5 μM	52.7 nM	[30]
Amperometric	~	0.6 μM	[31]
Adsorptive cathodic stripping voltammetry	0.1-1.2 μM	80 nM	[32]
Raman spectroscopy	~	~	[33]
Photoluminescence (PL) spectra	0.5 -30 μM	0.33 μM	[34]
Photochemical vapor generation atomic spectrometry	~	1nM	[19]
Amperometric	~	1nM	[23]
Fluorescence	0.20–80μM	4.3 nM	[35]
CE-LIF	~	0.023 ng/mL	[36]
Chemical sensor	0.01-100 μM	3.4 nM	[37]
Amperometry	1-100 μM	20 μM	[23]
Cyclic voltammetry	0.1-0.5 μM	80 nM	[28]
Cyclic voltammetry	0.0001-5 μM	0.0001 nM	[38]
Square wave voltammetry	0.05-1.0μM	30 nM	[39]
Chemiluminescence	1.0-30 μM	~	[40]
Fluorescence	0.003-10μM	3 nM	[41]
Fluorescence	3-30μM	~	[42]
Fluorescence	0-100μM	1.4 nM	[43]
NPs-based fluorescence	~	5.2 nM	[44]
NPs-based UV–visible spectroscopy	4.0-100μM	4.0 nM	[45]
NPs-based UV–visible spectroscopy	1.0-1000μM	30 nM	[46]
Differential pulse voltammograms	0.1-700 μM	30 nM	[47]
Amperometric	5 - 220 μM	0.22	48
Amperometric	50-500 mg L^{-1}	0.11 mg L^{-1}	49
Amperometric	0.15-20.3 μM	50 nM	This work

Compared with complicated and time consuming synthesis of other electrocatalyts or use of expensive instruments in the reported references, our present sensing method exhibited some advantages of simplicity, easy fabrication, fast analysis, and high sensitivity.

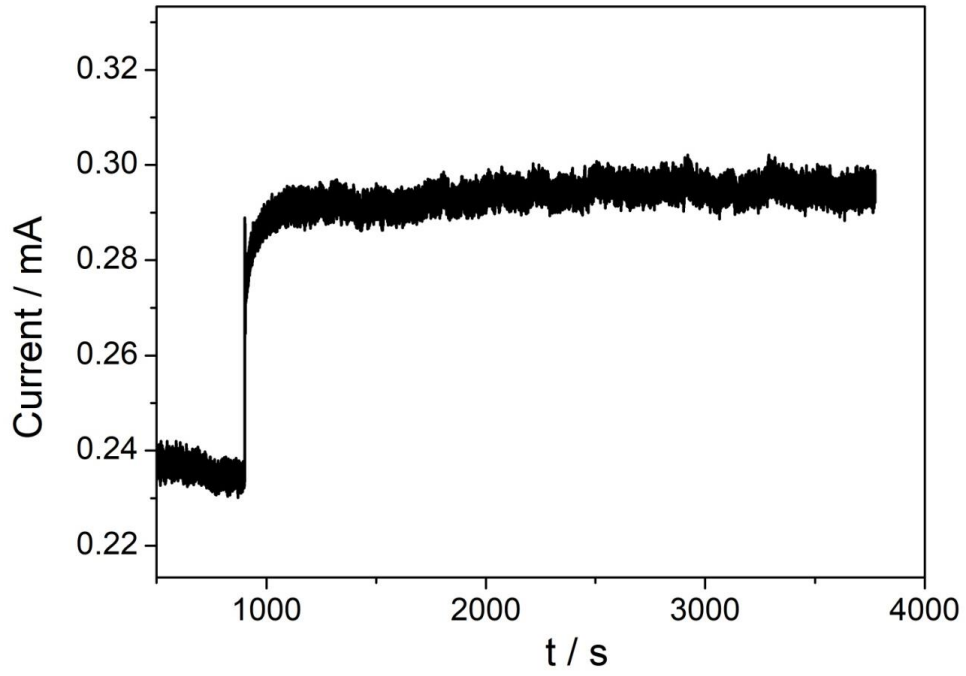

Figure 4. Long-term amperometric response of the Ni foam electrode to 2 μM His in stirred 1.0 M NaOH at an applied potential of 0.57 V.

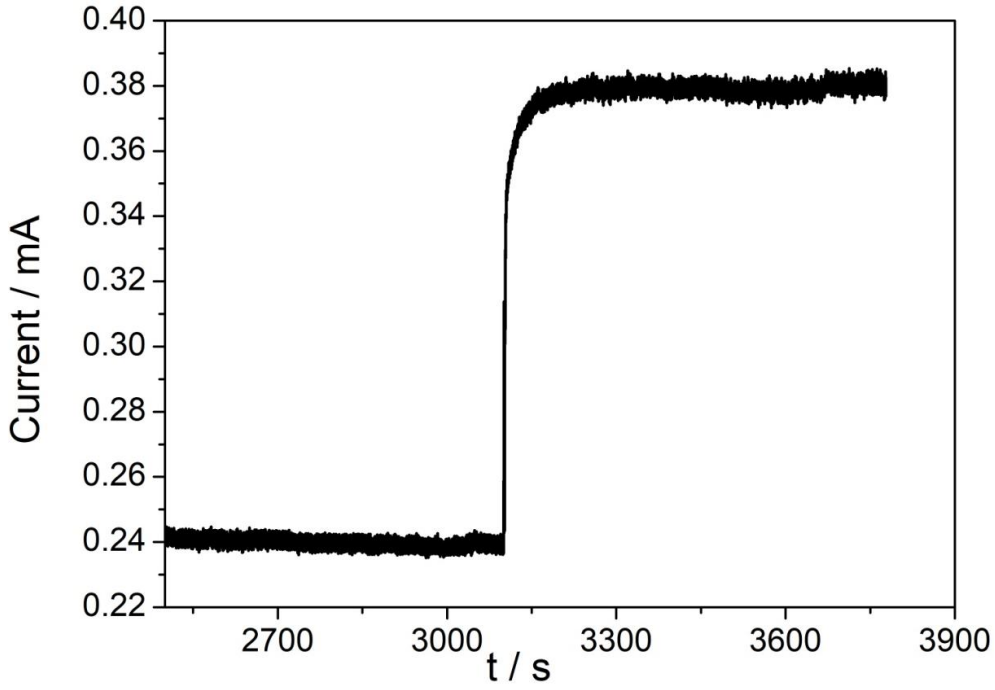

Figure 5. Long-term amperometric response of the Ni foam electrode to 6 μM His in stirred 1.0 M NaOH at an applied potential of 0.57 V.

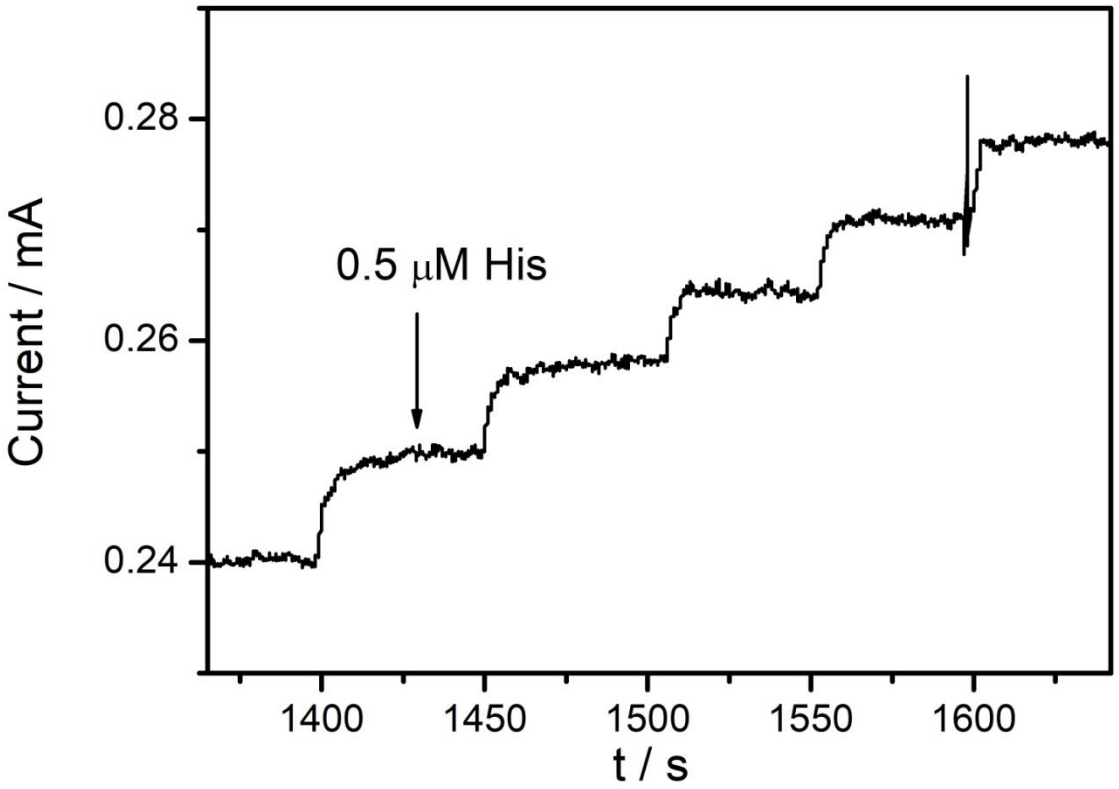

Figure 6. Repeatable test of the Ni foam electrode to the successive addition of 0.5 μM His in stirred 1.0 M NaOH at an applied potential of 0.57 V.

Fig. 4 and Fig. 5 show the long-term amperometric responses of the Ni foam electrode to 2 and 6 μM His, respectively. The result revealed that only 3% and 1% in the current value decreased even after 2800 and 600 s operation, respectively. Further more, after the electrode was stored in air for three weeks, it still remaied 80% of its initial value, indicating high stability of the electrochemical sensor. Repeatable measurements of the Ni foam electrode to the successive addition of His were also investigated. For five successive measurements of 12 μM His, the RSD of current response was 4.9%, as shown in Fig. 6. Reproducible experiments had been performed by using five parallel Ni foam electrode for the same solution of His, and the RSD of current response was found to be 6.7%, suggesting an acceptable reproducibility.

It is significant to test the anti-interference ability for electrochemical determination because the common interfering species including AA, UA, glucose, and GSH that coexist with His in physiological samples were easily oxidized. The interference experiments were studied by the successive addition of 2 μM His and 0.1 μM interfering species in 0.1 M NaOH at 0.57 V. The results indicated that the interferents were considered not to have interference on the electrochemical detection of His within the added ratio concentrations. This indicated that the electrochemical sensor exhibited ecellent selectivity for the analysis of His.

The practical applicability of the sensor was further validated by measuring the His spiked in human urine sample. 6 μL of urine samples containing spiked His was directly injected into the

continuous stirring alkline solution (10 mL) without pretreatment. The detection results were shown in table 2.

Table 2. The good analytical performances make it a promising method for the analysis of His in the clinical test.

Spiked concentration /μM	Detected concentration	Recovery
1.0	1.1	110%
2.0	1.9	95%

4. CONCLUSIONS

In this work, the commercially available three-dimensional porous Ni foam was firstly demonstrated for the electrochemical detection of His. The prepared electrochemical sensor exhibited excellent electrocatalytic performance with a detection limit of 50 nM and the linear range from 0.15 to 20.3 μM. The proposed method was also successfully employed to the detection of His in human urine sample. High sensitivity, fast analysis and simple preparation make this sensor promising for the analysis of His in the clinical test.

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