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pH-controlled electrocatalysis of amino acid based on electrospun cobalt nanoparticles-loaded carbon nanofibers

Yonghai Song, Zhifang He, Fugang Xu, Haoqing Hou*, Li Wang*

College of Chemistry and Chemical Engineering, Jiangxi Normal University, 99 Ziyang Road, Nanchang 330022, People's Republic of China

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ABSTRACT

Carbon nanofibers (CNFs) decorated with cobalt nanoparticles (CoNPs) were synthesized by a two-step procedure consisting of electrospinning and thermal treatment. The CoNPs–CNFs hybrid materials were characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction spectrum, which showed that the CoNPs were of the cubic phase and well dispersed on the surface of CNFs. The electrochemical behaviors and electrocatalytic performances towards the oxidation of the amino acids at the CoNPs–CNFs modified glassy carbon electrode (GCE) were evaluated. The results indicated that the CoNPs–CNFs showed good electrocatalytic activity towards the oxidation of cysteine and N-acetyl cysteine, and the current response of the CONPs–CNFs/GCE was sensitive to pH of the electrolyte solution. The peak current was quite large at pH 13.0 but greatly suppressed at pH 7.5, suggesting that the electrode can realize pH-controlled oxidation of amino acids. The good catalytic activity, well conductivity and high stability made the CoNPs–CNFs promising materials for constructing an enzymeless sensor.

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1. Introduction

The cobalt (Co)-based nanomaterials have attracted considerable attention due to their extensive applications in magnetoresistive devices [1], energy storage systems [2], electrochoromic thin films [3], heterogeneous catalysts [4] and electrocatalysis [5]. Especially, this multi-valence transition metal shows good electrocatalytic activity toward various compounds, such as ascorbic acid [6], acarbohydrates [7], and amino acids [8], and continues to attract great interest of researchers.

Many studies have reported that the electrocatalytic activity of Co-based materials used for biological and environmental sensing depended strongly on their architecture and polymorph [9–13]. To enhance their electrocatalytic activity, various architectures have been developed to obtain different polymorphs. For example, the Co hydroxide nanoparticles (NPs) were directly electrodeposited on glassy carbon electrode (GCE) in Na₂CO₃ solution in the presence of Co(II)-tartrate complex and showed good electrocatalytic activity toward oxidation of some amino acids [14]. The Co thin film electrodeposited on GCE in 0.02 M CoSO₄+0.1 M Na₂SO₄ solution was used as a novel electroactive material to detect ascorbic acid [6]. CoO NPs modified GCE have also been developed for sensing applications [15,16]. Carbon nanotubes —Co hybrid materials with improved electron transfer rate have been extensively used to construct various sensors [17–22].

Electrospinning, a new technique to generate fibers with the level of nanometer or even less, has attracted increasing interest [23]. Carbonization of these nanofibers at high temperature could be used to convert them into carbon nanofibers (CNFs). The two-step procedure consisting of electrospinning solution containing metal ion and subsequent carbonization have been used to construct CNFs decorated with metal NPs including PtNPs [24], NiNPs [25,26] and Pt/AuNPs [27] as electrode materials for sensing application. Compared with single-walled carbon nanotubes-metal NPs, the metal NPs-CNFs hybrid materials not only decorated on the CNFs surface but also inserted into the CNFs to form three-dimensional (3D) architectures, which would result in good electrocatalytic activity. These metal NPs-CNFs materials have been widely used to determinate formic acid [27], ethanol [25], glucose [26] and uric acid [24].

In this work, CNFs decorated with CoNPs was synthesized by first electrospinning of polyacrylonitrile/acetylacetone Co solution to obtain nanofibers, followed by carbonization of these nanofibers at high temperature under H₂. It is observed that the CoNPs–CNF nanocomposite modified electrode showed a pH-controlled electrocatalytic activity towards the oxidation of cysteine and N-acetyl cysteine. The CoNPs–CNF with good catalysis was used to fabricate an amino acid sensor, and its performance was investigated in detail.

^{*} Corresponding authors. Tel.: +86 791 8812086; fax: +86 791 8812086. E-mail addresses: hqhou@jxnu.edu.cn (H. Hou), lwang@jxnu.edu.cn (L. Wang).

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2. Experimental

2.1. Reagents and materials

Polyacrylonitrile (PAN, MW 269,000 g/mol), cobalt(II) acetylacetonate (Co(acac)₂), cysteine, N-acetyl cysteine, N,Ndimethylformamide (DMF), nafion (5%) and acetone were purchased from Sigma-Aldrich (Milwaukee, WI). Cetyl trimethyl ammonium bromide (CH₃(CH₂)₁₅N(CH₃)₃Br, CTAB) was obtained from Tianjin Yongda Chemical Reagents Development Company (Tianjin, China). Other reagents were purchased from Beijing Chemical Reagent Factory (Beijing, China). All reagents were of analytical grade and used as received. Buffer solutions were prepared with Na₂HPO₄, NaH₂PO₄ and NaOH to obtain pH values in the range of 7.5–13. Briefly, the phosphate buffer solution (PBS, 0.2 M) with pH 7.5-8.0 was prepared from 0.2 M Na₂HPO₄ and 0.2 M NaH₂PO₄. Buffer solutions with pH 9–12 were prepared by mixing 0.2 M Na₂HPO₄ and 0.1 M NaOH at different volume ratios. The 0.1 M NaOH was directly used as the electrolyte solution with pH 13. All solutions were prepared with ultra-pure water, purified by a Millipore-Q system (18.2 M Ω cm).

2.2. Preparation of the CNFs decorated with CoNPs

The CNFs decorated with CoNPs was fabricated by first electrospinning of PAN-Co(acac)₂ mixture solution to obtain PAN-Co(acac)₂ nanofibers, followed by carbonization of these nanofibers at high temperature (1000°C or 850°C) under H₂. The detail of the process was previously described [28]. Briefly, Co(acac)₂ was dissolved into DMF solution of PAN and the ratio of PAN to Co(acac)₂ was kept at 20% (wt.%). Then, CTAB (0.2 wt.%) and acetone (5 wt.%) was added into the mixed solution to reduce the surface tension and increase the conductivity of the solution. The as-prepared homogenous solution was electrospun by applying an electrical potential of 20 kV at a distance of 20 cm between the spinneret and the collector. In the electrical field of the order of 100 kV/m, the PAN–Co(acac)₂ nanofibers were formed. Finally, PAN-Co(acac)₂ nanofibers were converted into the CNFs decorated with CoNPs by carbonization at high temperature (1000 °C or 850 °C) under H₂.

2.3. Preparation of the CoNPs-CNFs/GCE

A defined amount of CoNPs–CNFs (about 1 mg) were suspended in 200 μ L ultra-pure water (containing 5 μ L nafion) and ultrasonicated for 30 min. Then a drop of the suspension (10 μ L) was cast on the surface of polished GCE and dried in an inverted beaker at room temperature. When the CoNPs–CNFs/GCE was not in use, it was stored in the inverted beaker at room temperature.

2.4. Measurements

X-ray diffraction (XRD) data were collected on a D/Max 2500 V/PC X-ray powder diffractometer using Cu K α radiation (λ = 1.54056 Å, 40 kV, 200 mA). The scanning electron microscopy (SEM) image was taken using a XL30 ESEM-FEG SEM at an accelerating voltage of 20 kV equipped with a Phoenix energy dispersive X-ray analyzer. Transmission electron microscope (TEM) image was recorded on a JEOL JEM-1011 TEM at 100 kV. The samples for SEM and TEM observation were prepared by placing 20 μ L CoNPs–CNFs suspension on a carbon coated copper grid, followed by drying at room temperature. The X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB MKII X-ray photoelectron spectrometer, using nanomonochromatized Mg K α radiation (photon energy = 1253.6 eV) as the excitation source and C1s (284.6 eV) as the reference line.

All electrochemical measurements were carried out on a CHI 660C electrochemical workstation (Shanghai, China) at the ambient temperature. The experiments were based on a conventional three-electrode system composed of a bare or modified GCE as working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl electrode in saturated KCl as reference electrode. The cyclic voltammetric experiments were performed in a quiescent solution. The amperometric experiments were carried out in a continuous stirring solution using a magnetic stirrer. 0.1 M NaOH was employed as the supporting electrolyte solution, purged with high purity nitrogen for 15 min prior to measurements and then a nitrogen atmosphere was kept over the solution during measurements.

3. Results and discussion

3.1. Characterization of the CNFs decorated with CoNPs

Fig. 1A showed a typical SEM image of as-prepared PAN-Co $(acac)_2$ nanofibers. As can be seen from the SEM image, the PAN–Co(acac)₂ nanofibers were smooth and dispersed randomly to form a 3D structure. The PAN-Co(acac)₂ nanofibers have a diameter ranging from 200 to 400 nm and a length of tens of micrometers. After they were carbonized at 1000 °C under H₂, the PAN-Co(acac)₂ nanofibers were transformed into CoNPs-CNFs and accompanied by a decrease of an average diameter, which was ascribed to the loss in total mass in the process of thermal treatment (Fig. 1B and D) [27,28]. The original fibers' morphology and 3D structure were maintained. Furthermore, a large number of CoNPs were formed and dispersed uniformly on the CNFs as shown in Fig. 1B and D. The CoNPs were firmly attached on the CNFs and hardly detached from the CNFs, since no CoNPs were observed in the background of the SEM image. The high-magnification image indicated that the CoNPs were in the range of 30-120 nm and the main size was about 55 nm (inset in Fig. 1B). Some CoNPs might also be embedded into the CNFs according to previous results [27,28]. Element analysis confirmed that the CoNPs was about 20.38% (wt.%). The 3D structure of CoNPs-CNFs could produce a large Co surface area which is helpful for its electrocatalytic performances. In fact, the size of CoNPs strongly depends on the carbonized temperature and is related to the diameter of CNFs. When the PAN-Co(acac)₂ nanofibers were carbonized at 850 °C under H₂, the size of CoNPs on the CNFs was obviously smaller than those obtained at 1000 °C but the diameter of CNFs was obviously thicker (Fig. 1C), which was unfavorable in producing a large surface area of CoNPs. The PAN-Co(acac)₂ nanofibers carbonized at 1100 °C under H₂ might produce bigger CoNPs that detached from the CNFs or evaporated at high carbonized temperature which resulted in the disappearance of CoNPs (data not shown).

The crystal structure and the phase purity of the as-prepared CoNPs–CNFs were characterized by XRD as shown in Fig. 1E. As can be seen in pattern a, there was only one broad diffraction peak around 25° . After thermal treatment, several new diffraction peaks at 44.5° , 51° and 75° were found (pattern b), which corresponded to the (1 1 1), (2 0 0) and (2 2 0) crystalline planes of fcc Co according to the standard spectrum of Co (JCPDS No. 15-806). The grain size of the CoNPs could also be calculated, considering the most intense peak in the XRD pattern of the CoNPs–CNFs, i.e., the peak at Co (1 1 1), by using the Scherrer's formula [29]:

$$d = \frac{\lambda}{B \cos \theta} \tag{1}$$

where λ and *B* are the wavelength of X-ray and full-width at half maximum intensity, respectively. It was found that the grain size of CoNPs was about 56.6 nm which was almost same to the result



Fig. 1. (A–C) SEM images of the PAN–Co(acac)₂ nanofibers (A) and CoNPs–CNFs by carbonizating at 1000 °C (B) and 850 °C (C). (D) TEM images of CoNPs/CNFs composites. (E) XRD patterns of the PAN–Co(acac)₂ nanofibers (a) and CNFs–CoNPs (b). (F) XPS spectrum of the PAN–Co(acac)₂ nanofibers (a) and CNFs–CoNPs (b). Inset in B: histogram showing the size distribution of CoNPs on CNFs.

obtained from the SEM results. As can be seen in pattern b, there was another characteristic diffraction peak at 31° , which should belong to (220) of Co₃O₄, suggesting that some Co₃O₄ NPs also formed on CNFs (JCPDS No. 42-1467).

Fig. 1F showed the XPS of the PAN–Co(acac)₂ nanofibers (curve a) and CoNPs–CNFs (curve b). For the XPS of the PAN–Co(acac)₂ nanofibers (curve a), typical peaks at 298.45 and 544.60 eV were attributed to C1s and O1s, respectively. After they were carbonized at 1000 °C under H₂, several new peaks appeared at 413.65, 778.25 and 793.18 eV, which were ascribed to N1s, Co2p_{3/2} and Co2p_{1/2},

respectively. The O1s peak at CoNPs–CNFs might mainly result from the Co₃O₄ NPs on CNFs, since some Co₃O₄ NPs also formed on CNFs.

3.2. Electrochemical properties of the CoNPs-CNFs/GCE

Fig. 2 showed the CV of as-prepared CoNPs–CNFs/GCE in 0.1 M NaOH. As can be seen in the figure, an oxidation peak at about -0.80 to -0.60 V was found (peak I), which attributed to the oxidation of Co(0) into Co(II) [30]. A pair of redox peak with formal potential $(E_{1/2} = (E_{pa} + E_{pc})/2)$ of +0.18 V were observed at about 0.20 V (peak



Fig. 2. CVs of CoNPs-CNFs/GCE in 0.1 M NaOH solution at 50 mV s⁻¹.

II). The oxidation peak located at 0.224 V might result from the oxidation of Co(II) into Co(III) [6]. The cathodic peak located at +0.171 V was ascribed to the reduction of the Co(III) [6]. The peak separation of ΔE_p was 53 mV, indicating the number of transfer electron was 1 [6].

Fig. 3A showed the CVs of CoNPs–CNFs/GCE in buffer solutions with different pH. As the pH decreased from 13.0 to 7.5, the peak potentials shifted positively and peak current density decreased gradually (curves a–g in Fig. 3A). As can be seen in Fig. 3B, the peak potentials linearly increased as the pH increased. The slope was evaluated to be about 107.54 mV/pH, indicating one proton transfer in the redox reaction in the pH range of 7.5–13.0 [6]. According to the above CV results and previous conclusion [30], the possible redox mechanism can be assumed as followed [30]:

$$\text{PeakI}: \text{Co}(0) + 2\text{OH}^{-} \rightarrow \text{Co}(\text{OH})_2 + 2e \tag{2}$$

 $PeakII: Co(OH)_2 + OH^- \rightarrow CoOOH + H_2O + e$ (3)

First, the metal Co(0) was transformed into $Co(OH)_2$ in the alkaline conditions (peak I) then further oxidized into CoOOH as potential shifted to the positive direction (peak II). The CoOOH can be used as heterogeneous catalysts and showed good chemical stability and electrocatalytic activity [31].

Fig. 3C showed the CV behavior of the CoNPs–CNFs/GCE at pH of 13 (curve a) and 7.5 (curve b) in the potential range from 0.0 to 0.60 V. It was found that the CV peak current density of the CoNPs–CNFs/GCE was very sensitive to the pH of buffer solutions. The peak current density was quite large at pH 13.0, while it decreased drastically at pH 7.5 (Fig. 3C), which indicated that the CNFs–CoNPs/GCE can be used as an "on–off" electrode by a pH-control. At pH 13.0, the electrode was at "on" state (Inset in Fig. 3C). At pH 7.5, the CV peak current density could hardly be observed, and the electrode was at "off" state (inset in Fig. 3C). This pH-controlled "on–off" behavior of the electrode was reversible. The CV peak current density could periodically change between pH 13.0 and pH 7.5 by controlling the solution pH.

Fig. 4A showed the CVs of CoNPs–CNFs/GCE at scan rates varied from 10 to 450 mV s⁻¹ in 0.1 M NaOH solution. Obviously, the peak current density was enhanced with the increasing of the scan rate. The peak current density was proportional to the scan rate at 10–450 mV s⁻¹ (Fig. 4B), indicating that the electron transfer reaction involved with a surface-confined process. It was noticeable that peak separation of ΔE_p was not zero but gradually increased as the scan rate increased (Fig. 4C), which could be ascribed to the possible mechanism involving in the direct electrochemical process. Generally, the direct electron transfer is known to be



Fig. 3. (A) CVs of CoNPs–CNFs/GCE in buffer solutions with different pH: 13.0 (a), 12.0 (b), 11.0 (c), 10.0 (d), 9.18 (e), 8.0 (f) and 7.5 (g). (B) Plot of the peak potentials and peak current density versus pH. (C) CVs of CoNPs–CNFs/GCE in buffer solutions with pH 13.0 (a) and 7.5 (b). The scan rate: 50 mV s⁻¹. Inset: Dependence of the peak current density (j_{peak}) on the cycle number when the pH was switched between pH 13.0 (\Box) and 7.5 (\blacksquare). Buffer solutions were prepared with Na₂HPO₄, NaH₂PO₄ and NaOH to obtain pH values in the range of 7.5–13.

strongly dependent upon a combination of interfacial electrostatic and chemical interactions. When the electro-active species were immobilized on electrode surface, the peak separation should be zero. However, the metal Co was firstly transformed into $Co(OH)_2$ in the alkaline conditions and then the $Co(OH)_2$ would be further oxidized into CoOOH as the potential shifted more positive. The $Co(OH)_2/CoOOH$ was not oriented or firmly immobilized on GCE surface but might be in various conformations [14].

The electron-transfer coefficient (α_s) and electron-transfer rate constant (k_s) could be determined based on Laviron theory [32]:

$$E_{pc} = E^{o'} + \frac{RT}{\alpha snF} - \frac{RT}{\alpha snF} \ln \nu$$
(4)



Fig. 4. (A) CVs of CoNPs–CNFs/GCE in 0.1 M NaOH solution at scan rate from 10 to 450 mV s^{-1} . (B) Plot of peak current density versus the scan rate from 10 to 450 mV s^{-1} . (C) Plot of the peak potential versus the natural logarithm of scan rate (ln ν).

$$E_{pa} = E^{o'} + \frac{RT}{(1 - \alpha s)nF} + \frac{RT}{(1 - \alpha s)nF} \ln \nu$$
(5)

where *n* is the electron transfer number, *R* is the gas constant (*R*=8.314 J mol⁻¹ K⁻¹), *T* is the temperature in Kelvin (*T*=298 K) and *F* is the Faraday constant (*F*=96493 C mol⁻¹). Fig. 4C showed the plot of peak potential (*E_{pc}*, *E_{pa}*) versus the natural logarithm of the scan rate (ln *v*). The anodic electron transfer coefficient, $\alpha_{s,a}$, and the cathodic electron transfer coefficient, $\alpha_{s,c}$, were calculated to be 0.61 and 0.54, respectively. This indicated the rate-limiting steps for the reduction and oxidation processes were different from each other [33]. The mean value of α was 0.58 and *n* was estimated to be

1, which further demonstrated a single electron transfer progress. When $n\Delta E_p < 200 \text{ mV}$, the electron transfer rate k_s could be estimated with the Laviron's equation $k_s = \alpha nFv/RT$ [32]. When the scan rate was 50 mV s^{-1} , the mean value of k_s was calculated to be 1.13 s^{-1} , which is larger than the electrodeposited Co_3O_4 NPs modified GCE (1 s^{-1}) [30] and the cobalt hydroxide NPs modified GCE (0.28 s^{-1}) [14]. The larger value of electron-transfer rate constant not only resulted from good conductivity of CNFs–CoNPs, but also from the 3D architecture of CoNPs–CNFs/GCE. The average surface concentration of electro-active CoNPs (Γ^* , mol cm⁻²) could be estimated by Faraday's law [34]:

$$p = \frac{nFQv}{4RT} = \frac{n^2 F^2 A \Gamma^* v}{4RT} \tag{6}$$

which can come to the expression as follows:

$$\Gamma^* = \frac{Q}{nFA} \tag{7}$$

where Γ^* is surface coverage of the redox species and v is the potential scan rate, A is the electrode surface geometrical area, n represents the number of electrons revolved in reaction and other symbols have their usual meaning. The calculated value of Γ^* was about 1.54×10^{-10} mol cm⁻² for CoNPs–CNFs/GCE.

3.3. pH-controlled electrocatalysis of amino acid

The sensing applications of CoNPs-CNFs/GCE were investigated. Fig. 5A showed the CVs of different electrodes in 0.1 M NaOH in the presence (curves b-e) and absence (curve a) of 5 mM cysteine. In the presence of 5 mM cysteine, the oxidation peak at about 0.55 V obviously increased at the CoNPs-CNFs/GCE (curve e) as compared with that in absence of cysteine (curve a). There was no obvious oxidation peak at bare GCE (curve b) and the CNFs/GCE (curve c). The oxidation peak at 0.55 V was much smaller at CoNPs/GCE (curve d) as compared with that of the CoNPs-CNFs/GCE. These results implied that the catalytic current mainly resulted from CoNPs toward catalytic oxidation of cysteine. Actually, CNFs played a crucial role in the performance of the sensor and provided a large surface area to increase the quantity of CoNPs and to reduce the dimension of the electrodeposited CoNPs. The large surfaceto-volume ratio of the small CoNPs produced a large total surface area that provided more chance to contact amino acids. As shown in Fig. 5B, the anodic peak current density related to the oxidation of Co(III) species increased in the presence of 5 mM cysteine (curve b) and N-acetyl cysteine (curve c) and the corresponding cathodic currents decreased compared to that in the absence of amino acids (curve a), which is typical catalytic reaction. This indicates that these amino acids are oxidized by active Co(IV) species with cyclic mediation redox processes. The proposed mechanism for this behavior is an EC' process according to the literatures [14,35]. In this mechanism, Co(III) species is oxidized to Co(IV) and then Co(IV) species accordingly oxidizes these amino acid followed by the regeneration of Co(III) species [21].

The pH-controlled electrochemical behaviors of the CoNPs–CNFs/GCE could be used to modulate electrocatalytic oxidation of amino acids. At pH 13.0 (0.1 M NaOH), there are obvious catalytic current in the presence of 5 mM cysteine (curve b in Fig. 5B) and 5 mM N-acetyl cysteine (curve c in Fig. 5B) as compared to that in the absence of amino acids (curve a in Fig. 5B). The electrocatalytic current density j_{pa} was relatively large and the electrocatalysis was in the "on" state (Fig. 5C). At pH 7.5 (0.2 M PBS), the oxidation current density in the presence of 5 mM cysteine (curve e in Fig. 5B) and 5 mM N-acetyl cysteine (curve f in Fig. 5B) were almost the same with that in the absence of amino acids (curve d in Fig. 5B). The j_{pa} was smaller and the electrocatalysis was in the "off" state. The pH-controlled electrocatalysis was also



Fig. 5. (A) CVs of different electrodes in 0.1 M NaOH in the presence (b–e) and absence (a) of 5 mM cysteine: (b) bare GCE, (c) CNFs/GCE, (d) CoNPs/GCE, (a and e) CoNPs–CNFs/GCE. (B) CVs of CoNPs–CNFs/GCE in buffer solution with pH 13.0 (a–c) and 7.5 (d–f) in the absence (a and d) and presence of 5 mM cysteine (b and e) and 5 mM N-acetyl cysteine (c and f). The scan rate: 50 mV s⁻¹. (C) Dependence of the electrocatalytic current density (j_{pa}) on the cycle number when the pH was switched between pH 13.0 (\bigcirc) and 7.5 (\spadesuit).

reversible, and the "on-off" behavior of the CoNPs-CNFs/GCE could be repeated for several cycles between pH 13.0 and 7.5 (Fig. 5C).

Amperometric measurements were carried out at 0.55V at CoNPs-CNFs/GCE by successive injection of cysteine (Fig. 6A) or N-acetyl cysteine (Fig. 6B) to a stirring 0.1 M NaOH. The oxidation current increased rapidly to achieve 95% of the steady state



Fig. 6. A typical steady-state response of the sensor to successive injection of cysteine (A) and N-acetyl cysteine (B) into stirring 0.1 M NaOH. The insets were the corresponding calibration curve. The applied potential was 0.55 V.

current within 2 s. The oxidation current density was proportional to the concentration of cysteine in the range of 1.2-24.8 mM (r=0.9910) with a slope of 77.50 µA cm⁻² mM⁻¹, as shown in the inset of Fig. 6A. The detection limit was estimated to be 0.14 mM based on the criterion of a signal-to-noise ratio of 3. The inset of Fig. 6B showed the calibration curve of the sensor to N-acetyl cysteine detection. The linear range of the N-acetyl cysteine detection was from 0.48 mM to 19.04 mM (r=0.9929) with a slope of 65.63 µA cm⁻² mM⁻¹. And the detection limit was 60 µM based on the criterion of a signal-to-noise ratio of 3.

For comparison, the amperometric response of the CoNPs/GCE towards the oxidation of cysteine and N-acetyl cysteine were investigated and the parameters were shown in Table 1. The comparison between CoNPs-CNFs/GCE and CoNPs/GCE in Table 1 declared that CoNPs-CNFs/GCE possessed a better catalytic activity and sensitivity towards the oxidation of cysteine and N-acetyl cysteine. The good catalytic activity and sensitivity might result from the large surface area of CoNPs-CNFs/GCE. Furthermore, since the results have been normalized as current density by the surface areas of CoNPs, the current density of CoNPs-CNFs/GCE was still larger than that of CoNPs/GCE, both to the oxidation of cysteine and Nacetyl cysteine. The good catalytic activity might also result from the synergetic effect between CNFs and CoNPs. Up to now, many sensors have been developed based on CoNPs for the detection of amino acids, and all of them have some advantages and limitations [14,36,37]. A comparison of the performance of our newly designed sensor with those already reported in literature regarding the performance of the two amino acids assay is also shown in

Table 1

Comparison of the performance of various amino acid sensors constructed from CoNPs.

	Compound	Detection limit (mmol L ⁻¹)	Linear range (mmol L ⁻¹)	Slope ($\mu A cm^{-2} mmol L^{-1}$)	References
CoNPs-CNFs/GCE	Cysteine	0.14	1.2-24.8	77.50	This work
	N-acetyl cysteine	0.06	0.48-19.04	65.63	This work
CoNPs/GCE	Cysteine	0.59	1.60-10.3	9.76	This work
	N-acetyl cysteine	0.41	2.42-11.17	10.99	This work
Co(OH) ₂ NPs/GCE	Cysteine	0.062	0.0625-0.476	2.4312 μA mmol L ⁻¹	[14]
	N-acetyl cysteine	0.22	0.245-1.01	$1.6672 \mu A mmol L^{-1}$	[14]
CoNPs/graphene/GCE	Cysteine	0.89	1.10-12.3	21.22	[36]
	N-acetyl cysteine	0.89	2.42-10.67	18.25	[36]
Cobalt oxyhydroxide/GCE	Cysteine	-	0.7-4	-	[37]

Table 1. Taking Co(OH)₂ NPs-GCE [14] as an example, the detection limit was pretty low (0.062 mM). While, the linear range was rather narrow (0.0625–0.476 mM). Recently, CoNPs decorated graphene modified GCE were constructed for the detection of amino acids with a detection limit of 0.89 mM and a linear range of 1.1–12.3 mM to cysteine and with a detection limit of 0.89 mM and a linear range of 2.42–10.67 mM to N-acetyl cysteine [36]. Compared with those sensors, the linear response range, the sensitivity and detection limit for amino acids detection of the resulted sensor in this work were much better than some other results.

Interference is inevitable in the determination of some analytes. Some interference was also investigated in our work. Chemicals such as saturated IO_3^- , saturated BrO_3^- , SO_4^{2-} , SO_3^{2-} and Fe^{3+} in fivefold concentration showed no interference to determination of cysteine, while SO_3^{2-} in a twofold concentration showed obvious interference to the oxidation of N-acetyl cysteine. These results implied the good selectivity of CoNPs–CNFs/GCE.

3.4. Reproducibility and stability of the CoNPs-CNFs/GCE

The stability of the sensor was also investigated. After the electrode was stored in the inverted beaker at room temperature for 10 days, the current response of the sensor to 1.0 mM cysteine and N-acetyl cysteine kept 97.3% and 97.5% of the original current, respectively. The reproducibility of the current signal for the same electrode to 1.0 mM cysteine was examined in 0.1 M NaOH. The relative standard deviation (RSD) was 5.3% for five successive measurements. The electrode-to-electrode reproducibility was determined in the presence of 1.0 mM N-acetyl cysteine with five different electrodes, which yielded a RSD of 5.7%.

4. Conclusions

The CoNPs–CNFs hybrid materials were synthesized using a two-step procedure consisting of electrospinning and thermal treatment. The CoNPs dispersed uniformly on the CNFs surface or embedded into the CNFs. The CoNPs–CNFs hybrid materials were used as electrode materials to prepare CoNPs–CNFs/GCE. The good conductivity, excellent electrocatalytic activity and porous structure of CoNPs–CNFs/GCE were favorable for sensing applications and were used to fabricate an enzymeless sensor for the pH-controlled electrochemical oxidation of cysteine and N-acetyl cysteine. The materials modified electrode showed a high sensitivity, wide linear range and good stability, thus it is considered to be an ideal candidate for practical applications.

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Biographies

Yonghai Song received his Ph.D. in analytical chemistry from the Changchun Institute of Applied Chemistry, Chinese Academy of Science, China. He is currently working as an associate professor at Jiangxi Normal University. His current research interests focus on biosensors.

Zhifang He received her science bachelor in chemistry in 2009 from Luoyang Normal University, China. She is working for her master's degree in Jiangxi Normal University, China. Her researcher interests are nano-materials and their applications in sensor.

Fugang Xu received his Ph.D. in analytical chemistry from the Changchun Institute of Applied Chemistry, Chinese Academy of Science, China. He is currently working as an associate professor at Jiangxi Normal University. His current research interests include nanostructured functional materials and their application for biosensors.

Li Wang received his Ph.D. in analytical chemistry from the Changchun Institute of Applied Chemistry, Chinese Academy of Science, China. She is currently working as a professor at Jiangxi Normal University. Her current research interest is focused on electrochemical sensors.

Haoqing Hou received his Ph.D. in chemistry from the Changchun Institute of Applied Chemistry, Chinese Academy of Science, China. He is currently working as a professor at Jiangxi Normal University. His current research interests include carbon nanofibers and their application for biosensors.