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An electrochemical impedimetric sensor based on biomimetic eletrospun nanofibers for formaldehyde

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Abstract

Herein, simple molecular recognition sites for formaldehyde were designed on electrospun ploymer nanofibers. In order to improve the conductivity of the electrospun ploymer nanofibers, carbon nanotubes were introduced into the resultant nanofibers. By employing these functionalized nanocomposite fibers to fabricate the biomimetic sensor platform, obvious change caused by recognition between recognition sites and formaldehyde moleculars was monitored through electrochemical impedance spectroscopy (EIS). The experiment conditions were optimized and then the quantitative method for formaldehyde in low concentration was established. The relative results demonstrated the sensor based on biomimetic recognition nanofibers displays an excellent recognition capacity to formaldehyde. The linear response range of the sensor was between 1×10^{-6} mol•L^{-1} and 1×10^{-2} mol•L^{-1}, with the detection limit of 8×10^{-7} mol•L^{-1}. The presented research provided a fast, feasible and sensitive method for formaldehyde with good anti-interference capabilities and good stability, which could meet the practical requirement for formaldehyde assay.

Key words: electrochemical impedance spectroscopy, biomimetic recognition, formaldehyde, electrospun nanofibers, ploy(methacryloylhydrazide)

Introduction

Highly selective recognition is one of biological functions in the natural system, including immune reaction and enzymatic processes. However, there were inherent limitations with respect to expensive, limited life and stability[1]. Therefore, to overcome these limitations, in recent years, material scientists and engineers drew the inspiration from biological systems had attracted much focus to design economically and functionally efficient biomimetic receptors allowing for substrate binding characteristics similar to natural systems[1,2]. In the biomimetic recognition systems included an indicator molecule which carried a suitable binding site and the analyte-receptor types involved various interactional methods, such as hydrophobic interactions, affinity-based ones, hydrogen bonds, polar interactions and covalent interactions[2]. C=N bond formed from condensation of amino and carboxyl has been a superiors and attracted lots of attention as the relation of imines in realms of chemistry and biology[3]. This reaction is widely distributed in nature and possesses significance in many pharmacological activities, such as transformations of amino acid and the cofactor, pyridoxal (vitamin B_6) [4,5]. Biomimetic recognition materials with pre-designed recognition sites exhibit a quite promising application and have many obvious advantages in sensors field, including low cost, simplicity, and reliability[6-11]. For instance, the traditional molecule imprinted technology was widely used as the biomimetic recognition, due to the complementarities in recognition sites and shape, molecule imprinted polymers work as synthetic antibodies toward target molecules[6,9], including various metal ions[12], organic molecules[13] or bioorganic

molecules[14]. Herein, molecule imprinted polymers could be used to establish mimic biosensor with artificial and controllable recognition capability, resulting from its rich artificial recognition elements and highly sensitive sensing effect. However, the analytical properties of this kind sensor mainly depend on the quantity of effective recognition sites of the molecularly imprinted polymer film[9]. The main issues restricting biomimetic recognition technology are its relatively narrow response kinetic range, bulk monolith and large template size limitations[15]. By coating a quite thin polymer film on a support, it could permit target molecules access easily, however, the binding capacity in the same area of designed device decreases. So the sensitivity and the linear response of the mimic biosensor structured by this strategy always cannot achieve desired effect[15-18]. With respect to the improvement of mimic biological functions, nanostructure materials with abundant recognition sites are dramatically appealing. Due to higher specific surface area, nanostructures for biomimetic recognition are believed to have better performance than the larger scales.

As well known, preparation of sensing materials in form of nanostructures may significantly improve the performances in the sensing devices and open the door to new types of applications. Electrospinning, which is an interesting and well-characterized physical phenomenon, opens new economically viable possibilities to produce nanofibers (NFs) with high-quality and low cost. Electrospun nanofibers are featured with large specific surface area, high porosity, which made them highly attractive to different applications in filtration, drug delivery platform, tissue engineering and so on. However, till now, there were rare reports about employing

electrospun nanofibers, which can enhance the recognition sites on the surface of the electrospining nanofibers, as the sensing element to fabricate the biomimetic sensor. Compared with traditional biomimetic materials, the prepared biomimetic recognition nanofibers exhibited superior features such as faster binding kinetics and higher target binding capacity. Moreover, to improve functions of nanofibers, electrospining technique has also been used to create various kinds of fibrous nanomaterials by adulterating other functional materials[19,20], such as nanoparticle, biomolecules and carbon nanotubes into the polymer nanofibers. Carbon nanotubes (CNTs) consist of seamless cylindrical graphitic sheets. As a sort of carbon nanomaterials with intriguing structures and unique preoperties[21], such as large specific surface area and capacitance, good conductivity and fast electron transfer rate, CNTs attracted intensive attention in lots of fields[22] for example composite materials, nanoelectronic devices. Compared to polymer/metal nanoparticles and other composite materials, the high aspect ratio of the carbon nanotube is beneficial to improve material percolation conductivity properties[23]. In our study, we proposed the new and facile electrospinning technology to create CNTs hybrid nanofibers to improve the biomimetic sensor performance.

Formaldehyde, a simple organic compound, is an important chemical found in many consumer products and works as a sterilising agent[24]. Formaldehyde has a great impact on human health, because of its potentially carcinogenic and mutagenic properties and its capability of forming intermediate and stable species of toxic and phototoxic radicals[13,25]. Thus, various quantitive methods for formaldehyde including

gas chromatogram, electrochemistry, chemiluminescence and piezoelectric sensor etc have been established[25-28]. Electrochemical impedance spectroscopy is a sensitive indicator of a variety of chemical and physical properties. Thus, impedimetric sensor, which owns the features associated with electrochemical approaches, namely the ability to be miniaturized, highly sensitivity, low cost of electrode mass production and cost effective instrumentation, etc, have attracted much attention, for example Liu et al reported room temperature impedance spectroscopy-based sensing of formaldehyde with porous TiO_2 under ultraviolet illumination[29] and others' invastigations[30,31]. However, to the best of our knowledge, limited impedimetric sensors have been developed to detect formaldehyde. Herein, the electrospun nanofibers for formaldehyde was designed and firstly employed as the bio-recognition element to fabricate biomimetic sensor based on electrochemical impedance spectroscopy. Benefited from the unique properties of electrospun biomimetic recogniton nanofibers, the impedimetric sensor prepared by this material exhibited obvious sensitivity, stability and selectivity towards formaldehyde. On this basis, this biomimetic impedimetric sensor based on biomimetic nanofibers was proposed for preparing new artificial biosensor with molecular recognition properties, which could be extended in environmental monitoring, food inspection and medical diagnosis and so on.

Experimental Section

Chemicals

Ploymethylmethacrylate (PMMA) was obtained from Sigma (St. Louis, MO, USA)

and used without further purification. Carbon nanotubes were purchased from Nanport. Co. Ltd. (Shenzhen, China). Other reagents were of analytical regents. The water used for the preparation of the solution was purified by a Water Purifier (China) purification system.

Instruments and measurements

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed with a CHI 760 electrochemical analyzer (Shanghai Chenghua Instrument Co., China). All electrochemical procedures were carried out with a three-electrode system comprising a platinum wire auxiliary electrode, Ag/AgCl reference electrode (sat. KCl) and a glassy carbon electrode (GCE, φ=3 mm) which served as the working electrode. Fourier Transform Infrared (FTIR) microscope was measured on a Nicolet 6700 FTIR spectrometer (Nicolet, USA).

Synthesis of ploy-methacryloylhydrazide (PMAH)

Ploy-methacryloylhydrazide was synthesized according to the previous report[32]. Briefly, PMMA was dissolved in dichloromethane. The reaction was carried out in 1:1 mixture of PMMA and hydrazine hydrate (n/n) with stirring at room temperature. The product was extracted with ethanol. At last, a white solid matter, PMAH, was obtained for the subsequent use.

Electrospinning

The homogeneous solution was prepared with dissolving 8 wt% PMAH into N,N-Dimethylformamide under magnetic stirring for 8 h. Then 0.5 wt% CNTs was

added into this solution, followed by vigorous stirring at room temperature for 16 h. PMAH/CNTs-NFs were fabricated by electrospinning utilizing a metallic needle to a conductive substrate at an applied electric voltage of 20 kV. The PMAH electrospun nanofibers (PMAH-NFs) were prepared according to previous process without adding CNTs.

Preparation of modified glassy carbon electrode

Before modification, the bare glassy carbon electrode (GCE, 3 mm in diameter）was polished with 0.3, 0.05 μm alumina particles on chamois leather in sequence and was washed sequentially with doubly distilled water, then it was sonicated thoroughly in ethanol and deionized water for 5 min and dried in air before use. For preparation of PMAH/CNTs-NFs modified electrode, 2 mg PMAH/CNTs-NFs was dispersed in 2:1 mixture of ethanol and DMF, and vigorous ultrasonication was employed. With a microinjector, 4 μL of PMAH/CNTs-NFs solution was deposited on the fresh prepared GCE surface, and kept in an oven at 60□ for 25 min. As a comparison, the PMAH-NFs modified electrode (PNFs/GCE) was similarly prepared. Then, the modified electrode was immersed in formaldehyde solution with different concentration for 60 s at room temperature. The EIS sensing strategy for the detection of formaldehyde was showed in scheme 1.

Results and Discussion

Principle of the biomimetic sensor

The biomimetic sensor was fabricated, as it shown in Scheme 1. Firstly, PMAH,

which owns the electrospun property, was synthetized. Then, in order to improve the electrochemical activity of the fabricated nanofibers, CNTs were introduced into the electrospun solution to fabricate biomimetic recognition elements. Secondly, the fabricated nanofibers with biomimetic function were immobilized onto the sensing matrix. Due to the interaction between formaldehyde and the fabricated PMAH electrospun nanofibers, which is nucleophilic addition reaction of carbonyl and amino, and the result produce is very unstable and easily lose H_2O then formed imine (Schiff base)[32,33], great change of electron transfer resistance at the biomimetic sensor was observed. Then, the biomimetic sensor for formaldehyde based on electrochemical impedance spectroscopy was obtained.

Characterization of PMAH

Figure 1A shows the scanning electron microscope (SEM) image which exhibits the nanofibers possess average diameter and are initially produced without large bead, and the CNTs do not appear on the surface of the nanofibers. Therefore, it presents that the appropriate tension of the complex for electrospining. Figure 1B displays the transmission electron microscope (TEM) image of the nanofibers, it can be obviously found that the CNTs in the nanofibers are well dispersed and the end of CNTs actually range in sequence at the surface of the nanofibers due to the effect of electric field, which can well avoid the physics absorption of the CNTs to target molecule. It`s well known the end of CNTs own highly electrochemical catalysis. Hence, the unique construction of this electrospun material possibly owns some advantages in establishing CNTs assisted biomimetic recognition sensor. Figure 1C shows the

typical FTIR spectrums of PMAH (a) and PMMA (b). Some characteristic absorption bands of PMMA (Figure 1b), such as the C-H asymmetric and symmetric stretching frequencies (2954 cm^{-1}), CH_2 bending vibrations (1435 cm^{-1}), and a broad intense band due to the stretching vibrations of the O-H groups from intercalated water were observed[10]. Comparing with Figure 1b, there was an evident stretching peak presented in 1244 cm^{-1} in Figure 1a, owing to the stretching characteristic peak of C-N[10]. It could strongly proved ploy-methacryloylhydrazide was successfully synthetized.

Electrochemical behavior of electrospun nanofibers modified electrodes

Different cyclic voltammograms of various modified electrodes in 5 mmol•L^{-1} $Fe(CN)_6^{3-}$ solution containing 0.1 mol•L^{-1} KCl are shown in Figure 2A. A classical pair of redox peaks is obtained at GCE. Due to the existence of insulative PMAH nanofibers on sensing interface, it works as a barrier to arrest the electron transfer between electrode surface and $Fe(CN)_6^{3-/4-}$. So the redox peak response at PMAH-NFs/GCE is obviously depressed. After CNTs are doped into the nanofibers, the current of redox peaks are recovered, which indicates that the good conductivity and high surface area of CNTs can improve the electrochemical activity of electrospun nanofibers[15,35]. With immersing in 0.01 mol•L^{-1} formaldehyde solution for 60 s, the redox peaks at the PMAH/CNTs-NFs/GCE is a slightly smaller than without, resulting from the molecular recognition sites of the PMAH/CNTs-NFs taken up by formaldehyde, then leading to the obstruction of the electron transfer between sensing interface and electrochemical probe.

Electrochemical impedance was also employed to characterize various modified

electrodes. In electrochemical impedance measurement, the semicircle obtained at high modulation frequency describes the Faradic electron-transfer process at the electrode interface, whereas the straight region obtained at the lower modulation frequency contains information about the diffusion-limited transport of the redox species in the electrolyte to the electrode interface. Figure 2B shows the electrochemical impedance spectra (EIS) of various electrodes in 5 mmol•L^{-1} $[Fe(CN)_6]^{3-/4-}$ containing 0.1 mol•L^{-1} KCl. It can be seen that a well defined semi-circle at higher frequencies is obtained at these electrodes. When PMAH nanofibers was modified on the surface of GCE, the impedance value was substantially increased and it was nearly forty thousand times greater than that case at GCE, suggesting that PMAH nanofibers blocked the charge migration between electrode surface and redox probe. However, when CNTs were doped into the nanofibers and were dropped onto GCE, the electron transfer resistance was effectively reduced. The present of CNTs, which have many high catalysis activity sites, could accelerate the charge migration. After PMAH/CNT-NFs/GCE was immersed in 0.01 mol•L^{-1} formaldehyde solution for 60 s, the impedance value increased, which was due to the molecular recognition sites of the PMAH/CNT-NFs plugged by formaldehyde, and led to the block effect of the charge migration between electrode surface and $Fe(CN)_6^{3-/4-}$. This phenomenon was similar to the performance of the cyclic voltammograms above.

Figure 3A shows Nyquist diagrams of electrochemical impedance spectra of various modified electrodes before and after recognizing formaldehyde. It can be seen that all

these electrodes obtained a well defined semi-circle at higher frequencies. The impedance value of PMAH-NFs/GCE incubated with 0.01 mol•L^{-1} formaldehyde solution for 60 s was remarkably higher than other electrodes. And the PMAH-NFs/GCE had a high impedance value. Whereas, when carbon nanotubes were doped into producing the electrospun nanofibers, the impedance value was remarkably decreased, due to the good conductivity of CNTs.

In order to take into account the resistance contribution from the specific interaction between formaldehyde and the sensing interface and improve the signal-to-noise and sensitivity, the changes in resistance were calculated according to the following expressions:

$$\frac{\Delta R}{R} = \frac{R^{*} - R}{R}$$

where R* and R represented the value of the electron transfer resistance of the modified electrode before and after the incubation with certain concentration of formaldehyde. The value of △R/R at PMAH/CNT-NFs/GCE was much higher than that case at PMAH-NFs/GCE, indicating carbon nanotubes doped into the nanofibers could improve the sensitivity of this biomimetic sensor.

As a kind of nanomaterials with inherent structures and unique properties, such as large specific surface area and capability, good conductivity and fast electron transfer rate, CNTs attracted intensive attention in lots of fields for example composite materials, nanoelectronic devices. Here, CNTs were used as functional material to improve the properties of electrospinning fibers. The EIS of PMAH and CNTs formed composite film modified electrode (PMAH/CNT/GCE) and the nanofibers containing

PMAH and CNTs (PMAH/CNT-NFs/GCE) before and after incubating with 0.01 mol•L^{-1} formaldehyde solution for 60 s were shown in Figure 3B. Compared curve a and b in Figure 3B, although these two modified electrodes had the same weight of CNTs and PMAH in the modified film, the EIS of these modified electrodes were apparently different. Attributing to the unique nanofiber construction of CNTs and PMAH formed composite, the smaller electron transfer resistance at these nanofibers modified electrode was observed. After incubating with 0.01 mol•L^{-1} formaldehyde solution for 60 s, the increased electron transfer resistance could be observed at both modified electrodes, indicating the ability of molecular recognition for formaldehyde at the sensing interface. It should be noticed that the larger increase of electron transfer resistance change is obtained at the nanofibers modified electrode, which demonstrated that the composite nanofibers own more molecular recognition sites and larger surface area.

Molecular Recognition of the electrospun composite nanofibers

Figure 4A shows that the impedance value of the PMMA-NFs/GCE is almost equate to that case at the PMMA-NFs/GCE electrode after incubating with 0.01 mol•L^{-1} formaldehyde solution for 60 s, indicating that PMMA which is usual molecule imprinted polymer[32,36,37], does not have specific recognition sites and obvious adsorption toward formaldehyde.

The electrochemical impedance response of the CNTs functionalized PMAH electrospun nanofibers modified electrode was expected to be affected by the amount of CNTs. As it depicted in Figure 4B, with the increased amount of CNTs in

fabricated nanofibers, an obviously decreased trend in electron transfer resistance was found. However, the further increased amount of CNTs in nanofibers did not remarkably depress the electron transfer resistance. Furthermore, the more CNTs would lead to the decrease of recognition sites on the nanofibers and the unwanted non-specificity adsorption. Considering the relationship between the value of ΔR/R and the amount of CNTs in the electrospun nanofibers, it was found that the introduction of CNTs into electrospun nanofibers could improve the molecular recognition effect; however, too much amount of CNTs would result in the poor recognition effect. Therefore, from the aspect of improving the analytical properties, the proper introduction of CNTs into the nanofibers was essential.

Optimum experiment conditions

The EIS of the modified electrode for certain concentration of formaldehyde was expected to be affected by the amount of the CNTs and PMAH formed composite nanofibers, which could be controlled easily. As shown in Figure 4C, the value of ΔR/R of this sensor was increased with increasing of PMAH/CNTs-NFs concentration from 1 mg/ml to 2 mg/ml. However, when the concentration was beyond 2 mg/ml, the value decreased, resulting from the imprinted nanofibers aggregated together and became thick membrane, then leading to slow diffusion of formaldehyde to the recognition sites [8].

It is well known that the preconcentration step was typically a simple and effective way for enhancing the sensitivity of the imprinted sensor. In order to determine the optimum operation time for formaldehyde detection, the relative experiment was

carried out. As it demonstrated in Figure 4D, with increasing of the preconcentration time, the value of the impedance was increased, resulting from formaldehyde took up the molecular recognition sites to hinder the charge migration between electrode surface and $Fe(CN)_6^{3-/4-}$. However, when the preconcentration time was over 60 s, the responses was nearly unchanged, indicating that nearly all of the recognition sites was taken up. Therefore, in order to obtain the strong electrochemical response, the optimized preconcentration time was 60 s.

Analytical application

Under the optimized conditions, the calibration curve for determination of formaldehyde was shown in Figure 5. With the increasing concentration of formaldehyde, the R_{et} value increased correspondingly, implying a higher amount of formaldehyde taken up the molecular recognition sites. ΔR/R was used as the measurement signal, as it deciphered in Figure 5B, the measurement signal was proportional to the logarithm of concentration of formaldehyde, ranging from 1 μmol•L^{-1} to 10 mmol•L^{-1}. The detection limit was 0.8 μmol•L^{-1}, which was lower than previous reports, as shown in Table 1. So the electrospun nanofibers based biomimetic hybrid film would emerge as a potential candidate for the biomimetic recognition elements, showing great promise for the construction of nanoscale biosensor.

The reproducibility of the resultant modified electrode before and after sensing formaldehyde were evaluated, as shown in Fig 5C. The relative standard deviation was calculated to be 6.6% and 2.5% estimated from the parallel response of five

different and freshly prepared electrode before and after immersing in 0.01 mol•L^{-1} formaldehyde-water solution, which revealed an excellent precision and acceptable repeatability in the construction of the sensor.

To evaluate the selectivity of the fabricated biomimetic sensor, some compounds and ions which could be possible interferences for formaldehyde liquid detection, were used to examine the selectivity of the resultant biomimetic nanofibers based sensor, as shown in the figure 5D. A foreign species was considered not to interfere if it caused a relative error <10% for the measurement of 0.01 mmol•L^{-1} formaldehyde. The results illustrated that the tolerated ratio of foreign substances to 0.01 mmol•L^{-1} formaldehyde was 50-fold for Cd^{2+}, Pb^{2+}, F^{-}, 100-fold for ethanol, methanol, carboxyl contained acetone. To further explore effect of compounds with aldehyde group, which could be potential interference in detection of formaldehyde, the acetaldehyde, butyraldehyde were chosen to examine their performance of electrochemical impedance spectroscopy. Then it was found that a little effect of acetaldehyde, but neglectable interference of butyraldehyde existed in detection process of formaldehyde, which indicated that the large activity of formaldehyde benefited to this nucleophilic addition reaction, while larger steric effect and weaker nucleophile would baffle this reaction[43]. As a whole, the response signal after recognition of formaldehyde was much larger than others'; which demonstrated the good selectivity of this sensor. All the merits of the biomimetic recognition sensor based on electrospun polymer nanofiber indicated that it might be sufficient for practical applications.

Conclusion

In summary, this work elucidated a new biomimetic sensing interface for formaldehyde based on electrochemical impedance spectroscopy. By combining electrospinning method and molecularly imprinted hybrid, compared with the traditional biomimetic materials, the proposed biomimetic nanofibers presented a porous matrix with very large surface area to volume ration, much more binding sites, and favorable binding characteristics, etc. Thus electrochemical impedance spectroscopy was employed for the first time in monitoring the change resulted from the target recognition took place at the binding sites on the surface of the nanofibers by the target molecules. The prepared biomimetic sensor obtained a wide dynamic response range with low limit of detection, ultra-sensitivity, satisfactory selectivity and excellent reproducibility. This strategy was simple and specific, and it could be coupled with other bio-recognition systems for other biological assays. Moreover, the flexible sensing platform not only acted as the sensitized sensing element for formaldehyde, but also offered a suitable carrier for immobilization of biomimetic recognition elements on the surface of electropinning nanofibers, which opens a promising approach to develop further electrospun nanofibers to establish biomimetic recognition sensor with favorable analytical performances.

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Table 1 Comparable figures of determining formaldehyde.

Methods	Reagents	Linear ranges	LODs	Refs
Electrochemical sensor	Pd nanowires	0.002-1 mmol•L^{-1}	0.5 μmol•L^{-1}	38
Electroanalysis	Pt nanoparticles Graphene	0-2 mmol•L^{-1}	40 μmol•L^{-1}	39
Enzymatic sensor	alcohol oxidase	0.06-0.46 mmol•L^{-1}	60 μmol•L^{-1}	40
Electrochemical sensor	Pt-Pd nanoparticles	0.010-1 mmol•L^{-1}	3 μmol•L^{-1}	41
Electrocatalysis	Pd nanoparticles	20-100 mmol•L^{-1}	10 mmol•L^{-1}	42
Electrochemical impedance spectroscopy	CNTs@PAMH-nanofibers	0.001-100 mmol•L^{-1}	0.8 μmol•L^{-1}	This work

Figure Legends

Scheme 1 Schematic routine of the biomimetic sensing platform for formaldehyde.

Figure 1 (A) the SEM image of PMAH/CNTs-NFs, (B) the TEM image of PMAH/CNTs-NFs, (C) FTIR spectra for (a) PMAH and (b) PMMA.

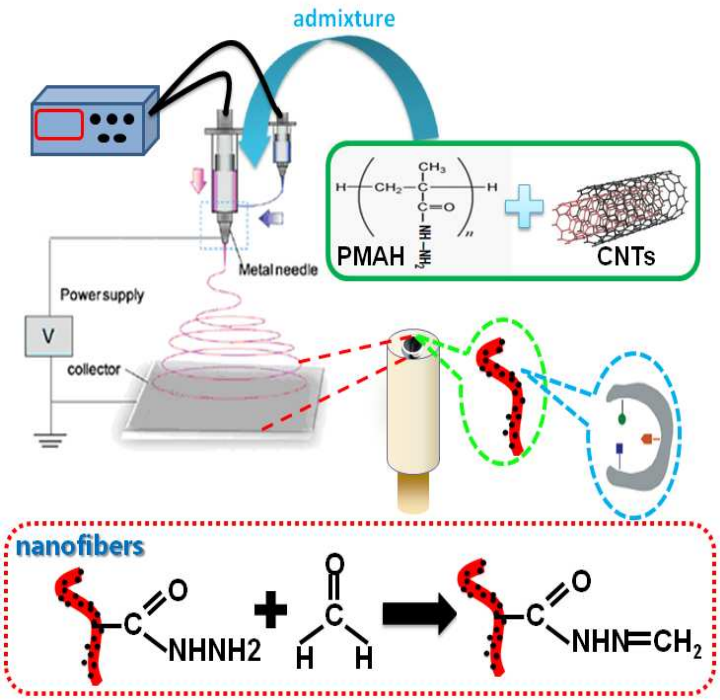
Figure 2 (A) Cyclic voltammograms of various electrodes in 5 mmol•L^{-1} $K_3Fe(CN)_6$ solution containing 0.1 mol•L^{-1} KCl. Scan rate: 100 mV·s^{-1}. (B) Nyquist diagrams of electrochemical impedance spectra of various electrodes. Electrolyte：5 mmol•L^{-1} $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol•L^{-1} KCl. Bare GCE (a), PMAH/CNTs-NFs/GCE (b), PMAH/CNTs-NFs/GCE incubated in 0.01 mol•L^{-1} formaldehyde solution for 60 s (c), and PMAH-NFs/GCE (d).

Figure 3 (A) Nyquist diagrams of PMAH/CNTs-NFs/GCE (a), PMAH/CNTs-NFs/GCE incubated in 0.01 M formaldehyde solution for 60 s (b), PMAH-NFs/GCE (c), PMAH-NFs/GCE incubated in 0.01 M formaldehyde solution for 60 s (d). (B) EIS of PMAH/CNTs/GCE (a), PMAH/CNTs-NFs/GCE (b), PMAH/CNTs/GCE (c) and PMAH/CNTs-NFs/GCE incubated with 0.01 mol•L^{-1} formaldehyde solution for 60 s (d). Electrolyte: 5 mmol•L^{-1} $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol•L^{-1} KCl.

Figure 4 (A) Nyquist diagrams of electrochemical impedance spectra of (a) PMMA-NFs/GCE and (b) PMMA-NFs/GCE incubated with 0.01 mol•L^{-1} formaldehyde solution for 60 s. (B) Effect of the amount of CNTs in the nanofibers on the sensing performance for 0.01 mol•L^{-1} formaldehyde in 5 mmol•L^{-1} Fe $(CN)_6^{3-/4-}$

solution containing 0.1 mol•L^{-1} KCl. (C) Effect of the amount of PMAH/CNTs-NFs on the sensing performance of as-prepared sensor for 0.01 mol•L^{-1} formaldehyde . (D) Impedance response for different times of preconcentration. Insert: impedance spectra corresponding to the PMAH/CNTs-NFs/GCE electrode immersed in 0.01 mol•L^{-1} formaldehyde-water solution at different time (the time increased from a to e in turn).

Figure 5 (A) Impedance spectrae of the PMAH/CNTs-NFs/GCE as the function of formaldehyde concentration [(a) 1 μmol•L^{-1}, (b) 10 μmol•L^{-1}, (c) 50 μmol•L^{-1}, (d) 3 mmol•L^{-1}, (e) 5 mmol•L^{-1}, (f) 10 mmol•L^{-1}] in 0.1 mol•L^{-1} KCl containing 5 mmol•L^{-1} $[Fe(CN)_6]^{3-/4-}$. (B) Calibration curve for the electronspun sensor. (C) Impedance spectra for 5 mmol•L^{-1} $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol•L^{-1} KCl at PMAH/CNTs-NFs/GCE before (a) and after immersing into 0.01 mol•L^{-1} formaldehyde solution for 60 s (b). (D) Selectivity of PMAH/CNT-NFs/GCE for 0.01 mol•L^{-1} formaldehyde, 0.5 mol•L^{-1} F^-, Cd^{2+}, Pb^{2+} and 1 mol•L^{-1} methanol, ethanol, acetone, butyraldehyde, acetaldehyde.



Scheme 1

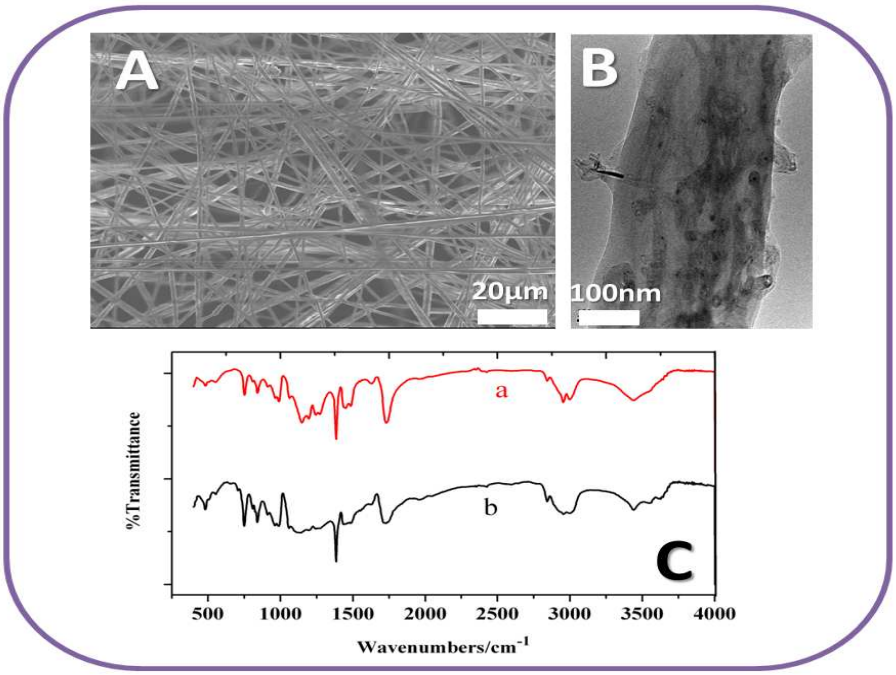


Figure 1

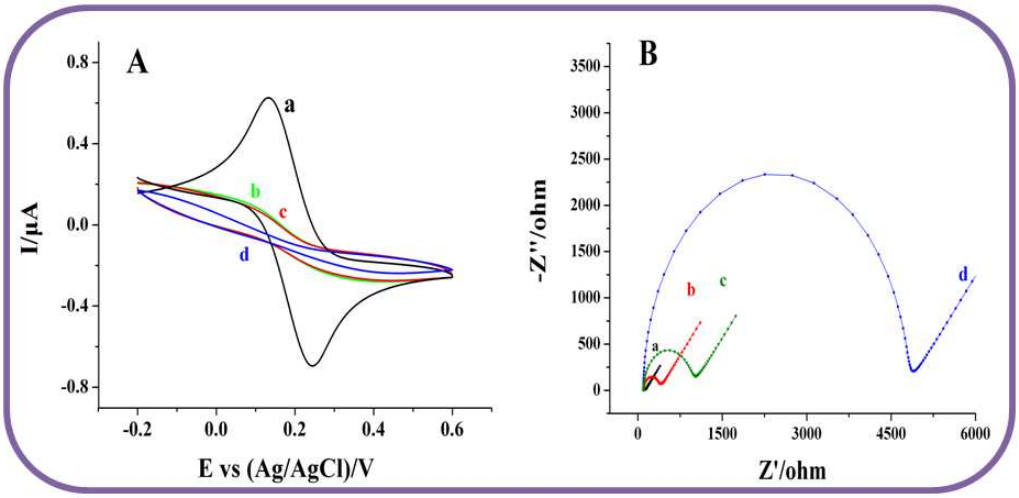


Figure 2

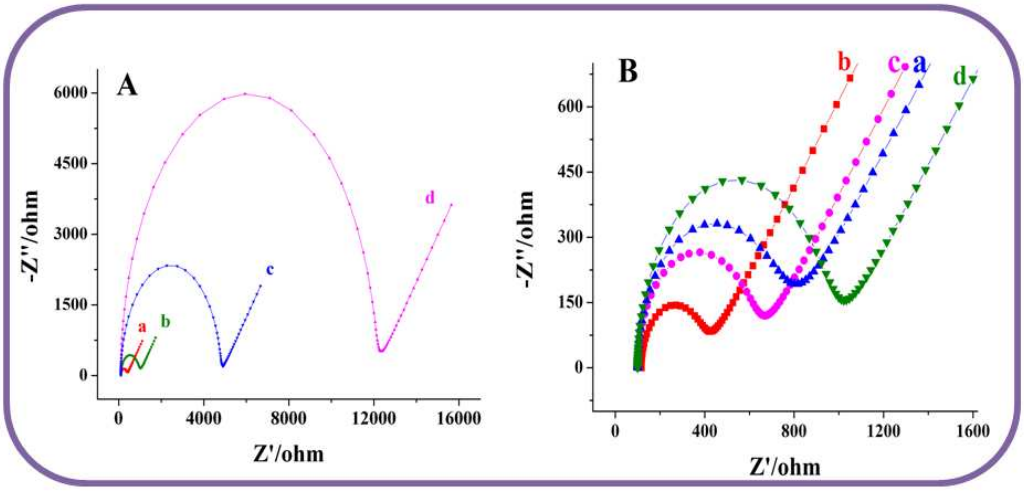


Figure 3

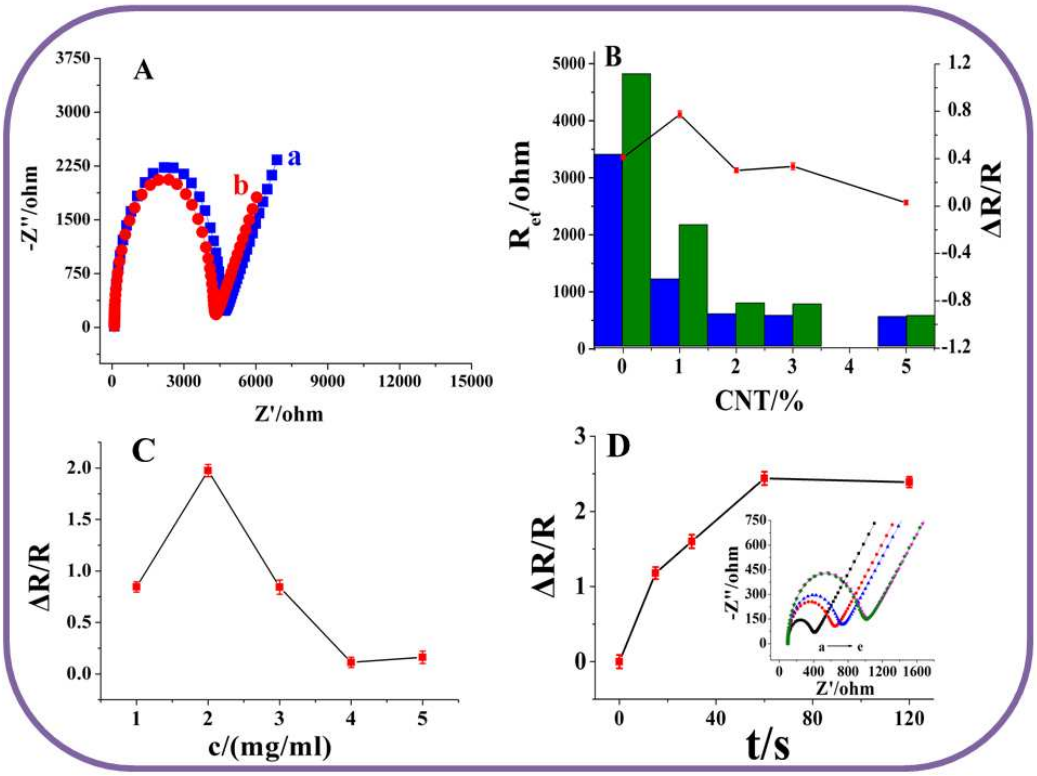


Figure 4

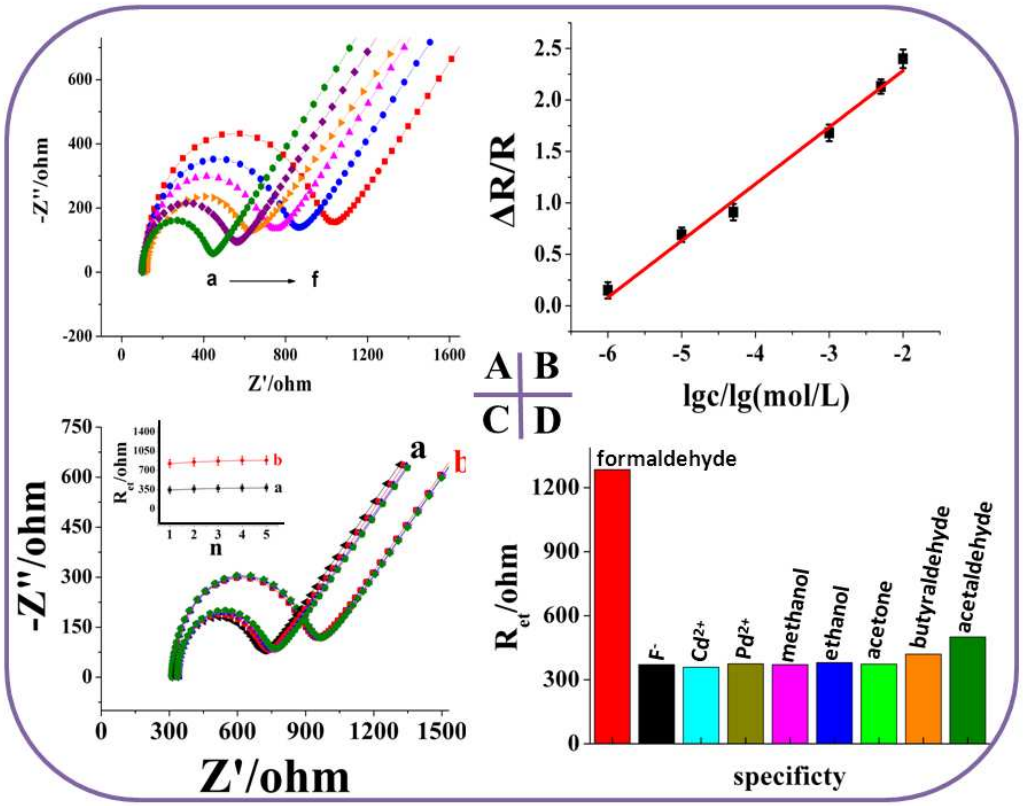


Figure 5