Preparation and application of a novel nitric oxide sensor by chemically nano-modified technology

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Electrochemical microsensors are concerned with chemically nano-modified technology and nanomaterials that exhibit large surface area and high catalytic activity. Recently, several nanomaterials such as carbon nanotubes (CNTs) [1], nano-Au [2], nanoalloys [3] and quantum dots [4] have emerged as a novel modifier for the preparation of chemical and biological sensors.

Carbon nanofibers (CNFs) are characterized as having high degree of orientation on their graphitic basal planes parallel to the fiber axis and possessing excellent mechanical strength and electrical conductivity [5]. They are also recognized as one of the promising materials based on its nanostructure and particular properties. Moreover, compared with CNTs, CNFs have larger surface-active groups-to-volume ratio, better mechanical stability and easier mass production. Especially, CNFs process more edge sites on the out wall than CNTs. Based on these advantages; the acid treated CNFs as a biocompatible electron conductor have been widely used in electroanalysis. CNFs can be modified onto the electrode surface by methods like casting, deposition, chemical vapor deposition and adsorption. These methods, however, generally lack film controllability and are not suitable for electrodes with small dimensions or special shapes.

In this work, we developed a novel method for immobilizing CNFs on the surface of carbon fiber microelectrodes (CFE) via a simple and well-controlled in situ modification technology. This was achieved by the stable dispersion of CNFs in alizarin red (AR) aqueous solutions and the subsequent immobilization on CFE by electropolymerization. The resulting PAR-CNF composite modified CFE exhibited an excellent electrochemical catalytic activity for the oxidation of nitric oxide (NO). This nano-modified electrode can be as a sensitive NO sensor. And it can be applied to the amperometric determination of NO in biosamples with high selectivity.

CFE was prepared as follows: carbon fibers (7.8 μm in diameter) were firstly cleaned by sonicating in acetone, alcohol and water, each for 3 min. The cleaned carbon fibers were connected to copper wires for conducting by silver glue and sealed in capillary. The effective length of carbon fibers was controlled to be about 800–1000 μm under the microscope for sensing. The obtained CFE was compared by sweeping from -0.2 to 0.8 V in 0.1 M KCl containing 2.0 mM $K_3[Fe(CN)_6]$ to make sure that all the employed CFE possessed the same effective surface area. Prior to surface modification, CFE was pretreated by sweeping from -0.8 to 1.0 V in 0.1 M H_2SO_4 for 20 cycles by cyclic voltammetry.

CNFs made hydrophilic by sonicating for 4 h in the mixture of H_2SO_4 (98%) and HNO_3 (36–38%) with the volume ratio of 3:1 followed by thorough rinsing with water. The treated CNFs were dried in vacuum oven and then kept in desiccator for future uses. CNF suspensions were prepared by sonicating CNFs in 5 mg/mL alizarin red aqueous solution for 10 h to form a final concentration

of 0.5 mg/mL.

The fabrication of PAR-CNF/CFE was carried out by potentially sweeping CFE in the range of 0 V~2.2 V at a scan rate of 50 mV/s for 25 cycles in aqueous solutions containing 5 mg/mL alizarin red and 0.5 mg/mL CNFs without any supporting electrolyte.

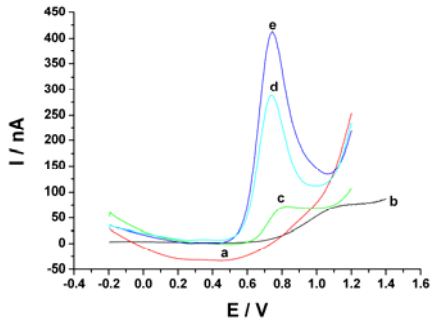

Fig. 1. Square wave voltammogramms of bare CFE (b), PAR/CFE (c) and PAR-CNF/CFE (a, d and e) in the absence of NO (a), and in the presence of 18 μM NO (b, c and d) and 36 μM NO (e) in 0.1 M deaerated phosphate buffer solution (pH 7.4).

Fig. 1 shows the square wave voltammogramms of different electrodes in the absence and presence of NO. When the concentration of NO was 18 μM, only a small and wide oxidation peak at 1.1 V with a current of 17.3 nA is observed (curve b) at bare CFE. The oxidation current is enlarged to 37.1 nA at PAR/CFE (curve c), along with the apparent negative shift of the oxidation potential to 0.8 V. However, a sharp oxidation peak at 0.74 V with a current of 273.6 nA is observed at PAR-CNF/CFE (curve d) and there is no electrochemical signal in the absence of NO (curve a). Moreover, the peak current increased to 353.4 nA when the NO concentration was added to 36 μM. These results suggest that the peak corresponds to the electrochemical oxidation of NO and the PAR-CNF film can catalyze the electrochemical oxidation of NO on CFE. This is probably attributed to the synergetic enhancement effect of PAR and CNFs for the electrochemical oxidation of NO. That is to say, the formation of a conductive porous structure of CNFs on CFE and the surface coating of CNFs by PAR produce a three-dimensional reaction network with plenty of electro-active centers, which possesses apparent advantages for enhancing the accumulation and improving the electrochemical response of NO in comparison with the compact PAR film on CFE.

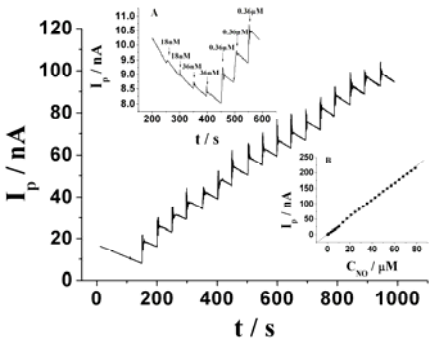

Fig. 2. Amperometric response of PAR-CNF/CFE with successive injections of different concentrations of NO at the operational potential of 0.85 V. Insert A: Amperometric response of low concentration NO. Insert B: plot of the dependence of the oxidation peak current on NO concentrations in the range of 36 nM ~ 78 μM.

Fig. 2 shows that the response of NO at PAR-CNF/CFE is rapid (~2 s) and has good reproducibility. The current response exhibits a good linear relationship with the concentration of NO in the range of 36 nM ~ 78 μM, along with a low detection limit of 18 nM (S/N=3). The PAR-CNF/CFE also has good stability: it remains 93% of its initial response after it was kept in air for ten days. Moreover, 100 times glucose, caffeine, L-arginine, L-glutamic acid, cholesterol and barbitone, 10 times uric acid and ascorbic acid have no interference on the determination of NO.

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