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Electroanalytical application of graphite nanofibers paste electrode

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ABSTRACT

This article reports on a new kind of carbon paste electrode prepared by mechanical mixing graphite nanofibers (GNF) with mineral oil. Electrochemical behavior of the as prepared graphite nanofibers paste electrode (GNFPE) were thoroughly evaluated with respect to the redox properties of some common electroactive compounds, such as ferricyanide, uric acid (UA), ascorbic acid (AA), dopamine (DA), catechol, acetaminophenol (AP), and epinephrine (EP). The characteristics of the GNFPE were also compared with those of the conventional graphite paste electrode (GPE). The results demonstrated that GNFPE provided improved electron-transfer kinetics than did GPE. In addition, GNFPE and GPE were tested as hydrogen peroxide and β-nicotinamide adenine dinucleotide (NADH) probes and the excellent experimental results further demonstrated the remarkable electrochemical advantages of GNFPE compared with GPE for analytical applications.

1. Introduction

Since the invention of polarography in the beginning of the last century, voltammetric methods have received great attentions in electroanalytical chemistry. Various techniques were proposed to promote the sensitivity (detection limit) over the past decades. In present days, however, the techniques are almost completed and the promotion of analytical performance (e.g. sensitivity, selectivity, and durability) is more and more depended upon the electrode material besides the modification methods of the electrode surface. A wide variety of new electrode materials have been explored in recent years, especially, carbon based materials [1]. For example, graphite [2], glassy carbon [3], carbon nanotubes (CNT) [4], ordered mesoporous carbon (OMC) [5], and diamond (doped) [6] are extensively employed as indicators (working electrodes) in the fundamental and applications of electrochemistry. Besides the carbon materials mentioned above, a new kind of carbon material, graphite nanofibers (GNF) have captured much attention owing to their thermal and mechanical stability, high electrical conductivity, large surface active groups, surface-to-volume ratio, low-ohmic resistance, and easy mass production. Especially, the unique surface properties make GNF very suitable in applications ranging from catalyst supports [7], smart composite materials [8], gas sensors [9], and novel electrode supports for redox liquid electrodes [10] to electrode materials for supercapacitors [11].

Graphite nanofibers have the lengths in the order of micrometers and the diameters ranging from several to ca. 200 nm. According to the anisotropic alignment of graphene layers, they were usually classified into three particular structures such as platelet, herringbone and tubular axis [12]. Presently, the size and graphite ordering can be well controlled when synthesizing [13]. Therefore, compared to carbon nanotubes (CNT), GNF process much more edge sites and active groups on the out walls and so, they may be more suitable to act as electrode materials for electrochemical sensing and biosensing. Chaniotakis et al. systematically compared different carbon materials, viz. GNF, CNT and graphite powder for the construction of glucose biosensors. The results demonstrated that GNF were the best matrixes for immobilizing proteins and enzymes for biosensor development [14]. Bala et al. reported that it was possible to detect NADH with a low detection limit of 11 μM by using GNF-modified glassy carbon electrode [15]. It was also reported that a GNF-modified electrode had been proved to have excellent catalytic activity towards the reduction of H_2O_2 and could be used for continuous monitoring of H_2O_2 with high sensitivity and good selectivity [16]. You et al. [17] reported that Pd/GNF composite modified electrode could be use for simultineous determination of DA, UA and AA. The proposed method was also applied to the determination of DA and UA in real samples with satisfactory results.

From the point of view of electrode construction, those mentioned systems were based on film coated electrodes which were prepared by casting microliters of GNF suspension (e.g. in DMF) on the conducting substrates. However, all those surface modified electrodes unavoidably suffered from serious disad-

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vantages, such as mechanical instability and electrode fouling during continuous measurements, relying upon another conducting substrate (e.g. GCE, Au and Pt) as support, complicated prepare procedures and lack of flexibility when dealt with the association of molecule recognition species (e.g. enzymes). In order to overcome the problems, we draw on the experience of the conventional carbon paste electrode (CPE) [18,19]. Herein, a new carbon paste electrode, graphite nanofibers paste electrode (GNFPE), was prepared by simply homogenous mixing GNF with mineral oil and then packed the resulting composite into a glass tube. Like CPE, the GNFPE showed a very stable electrochemical behavior and it could be surface renewable by simple polishing on weighing paper when contaminated and still kept its favorable electronic and electrochemical properties at the same time. Therefore, it can be used to study the electrochemistry of a wide range of molecules and for promising sensory applications. We also compared it with the conventional GPE in this work.

2. Experimental

2.1. Apparatus

Electrochemical measurements were performed with a CHI 660B electrochemical workstation (Chenhua Instruments Co., Shanghai, China). Three-electrode system was employed in this study. The electrodes were inserted into a 10 mL beaker through holes in its Teflon cover. A platinum wire and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. All potentials were referred to the latter. The composite electrodes (GNFPE and GPE) employed as working electrodes were prepared in the laboratory according to the procedure described below. A magnetic Teflon stirrer provided the convective transport during the amperometric measurements. All the experiments were performed at room temperature (20 ± 0.5 °C).

2.2. Reagents

Graphite nanofibers (GNF, diameter: 30–50 nm, length: 5–20 μm, purity: 95%), graphite powder (GP, size: 3–5 μm, purity: 99%), ascorbic acid (AA), uric acid (UA), acetaminophen (AP), β-nicotinamide adenine dinucleotide, reduced disodium salt hydrate (NADH), epinephrine (EP), dopamine (DA), catechol and mineral oil were purchased from Sigma–Aldrich. All other chemicals were analytical grade and used without further purification.

2.3. Electrodes preparation

The graphite nanofibers paste electrode (GNFPE) was prepared by thoroughly hand-mixing a suitable amount of graphite nanofibers and mineral oil in the ratio of 70:30 (w/w) in an agate mortar. Then a portion of the resulting paste was firmly packed into a cavity (3-mm diameter, 5-mm depth) of a glass tube. A copper rod was inserted to the glass tube from the rear to establish electrical contact. Graphite paste electrode (GPE) was prepared in a similar way except the graphite powder to mineral ratio of 70:30 (w/w). When necessary, the electrode surface can be refreshed by polishing the electrode on a weighing paper with satisfied repeatability. For example, the relative standard deviation (RSD) was found to be 2.1% for five times polishing the surface of the same GNFPE in 1 mM ferricyanide. A little worse reproducibility (RSD = 3.6%) was observed upon five identical prepared electrodes from the same batch with the same composition.

3. Results and discussion

3.1. Composition of the GNFPE

Electrochemical activities and analytical performance of carbon paste electrode were absolutely dependent upon its composition or the carbon to mineral oil ratio. Therefore, in order to acquire the optimum GNF/mineral oil value, we prepared several batches of graphite nanofibers paste electrodes (GNFPE) with different percentages of GNF (i.e. 40, 50, 60, and 70% (w/w)) and interrogated them with 1 mM potassium ferricyanide by cyclic voltammetry. Fig. 1 depicts the plots of peak potential separation (ΔE_p, A) and peak current (I_p, B) with respect to the paste composition. It can be seen that the ΔE_p value decreased and the I_p enlarged at the same time when the mineral oil percentage was diminished in the composition, demonstrating the electroanalytical response of the GNFPE was improved. This phenomenon can be explained by the fact that the paste electrode shows higher resistance that hinders the electron transfer with the increase in the mineral oil percentage.

The results confirmed that the best reversibility in terms of the lowest ΔE_p and largest I_p for $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple was obtained with a high ratio (w/w) GNF/mineral oil paste composition of 70/30 (w/w), which was in accordance with the previous work based on graphite/oil paste composition reported by Adams et al. [20,21], the carbon nanotube paste electrode [22], and the ordered mesoporous carbon paste electrode [23]. Much higher GNF/mineral oil ratio was not used just because the composite paste made was too dry and loose to be wedged through the glass tube. On the basis of the above optimization, the GNF/mineral oil ratio of 70/30 (w/w) was selected for subsequent work.

3.2. Potential window

One highlighted virtue of carbon or graphite based electrode is its wide potential window, which makes them very versatile in various fields of electrochemistry. Linear sweep voltammogram (LSV) was run in three typical deoxygenated media, viz. 0.10 M sulfuric acid, 0.06 M phosphate buffer (pH 6.85) and 0.10 M NaOH with a sweep rate of 50 mV/s. In neutral medium, the GNFPE showed the widest potential window of near 2.40 V in that the oxidation of the solvent starting at 1.45 V and the hydrogen evolution at potential more negative than −0.95 V. Under the acidic and alkaline conditions, the GNFPE exhibited the potential windows of 2.06 and 1.92 V, respectively. So the potential window of the GNFPE was

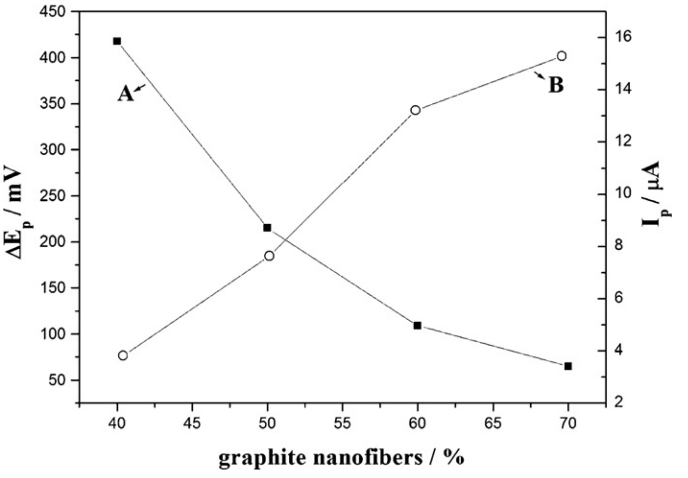

Fig. 1. The effect of the paste composition on the (A) peak potential separation (ΔE_p) and (B) peak current (I_p) of 1 mM ferricyanide in 0.1 M potassium chloride. Scan rate: 50 mV/s, compositions: 40/60, 50/50, 60/40, and 70/30 (w/w) (GNF/mineral oil).