

Graphene-Loaded Nanofiber-Modified Electrode: A Novel and Sensitive Electrochemical Detection System

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ABSTRACT

A novel electrode based on graphene/polyaniline/polystyrene (G/PANI/PS) nanofibers has been prepared via electrospinning for the determination of biomolecule (*i.e.* dopamine) and heavy metals (*i.e.* Cd²⁺ and Pb²⁺). The factors affecting the electrochemical sensitivity and morphology of G/PANI/PS nanofibers, such as percentage of G loading (%G), electrospinning time, type of organic solvent and concentration of polymer were investigated and optimized. The obtained nanofibers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and cyclic voltammetry (CV). The G/PANI/PS nanofiber-modified electrodes were used for selective and sensitive determination of dopamine. A very low limit of detection (LOD: 0.05 nM) and limit of quantification (LOQ: 0.30 nM) were achieved for dopamine. Furthermore, these modified electrodes were successfully applied for sensitive and simultaneous determination of Cd²⁺ and Pb²⁺.

Keywords: Graphene, Polyaniline, Nanofiber, Dopamine, Heavy Metal

1 INTRODUCTION

Electrochemical detection is an important technique for various fields of applications (*e.g.* medical diagnosis, food inspection, and environmental monitoring) because it is simple, rapid, inexpensive and portable. [1] However, the working electrodes are usually designed to be a small size. Thus, the surface area of the working electrodes is limited leading to low detection sensitivity. To increase the electrochemical sensitivity, electrode surface modification becomes a crucial step. Various types of nanomaterials have been used for the modification of working electrodes.

Recently G, a two-dimensional single atom thick of carbon nanomaterial has become a material of interest due to its remarkable properties, such as large surface area, high electron transfer and high electrical conductivity. [2, 3] Nonetheless, the use of pure G usually faces the agglomeration problem leading to limited applications. To solve this problem, conducting polymers are introduced to form the nanocomposite with G.

PANI is a promising material for electrode modification due to its high conductivity, high environmental stability and biocompatibility. [4, 5] It has been reported that G/PANI nanocomposite can be used to improve the electrochemical sensitivity in the detection of various molecules. [1, 4-7]

Electrospinning is a fabrication method for producing continuous fibers with diameter ranging from nanometer to micrometer. This technique can provide the high surface-to-volume ratio fibers with controlled morphology. It has been reported that electrospinning fabrication is used for electrode surface modification along with electrochemical detection systems. [8-10]

Dopamine (DA) is one of the most important natural catecholamine neurotransmitters. Abnormal levels of DA may result in neurological disorders, such as Parkinson's disease and Schizophrenia [11-14]. Due to its electrochemical activity, the development of new electrochemical detection systems for selective and sensitive determination of DA is still greatly required for medical diagnoses.

Heavy metals, such as lead and cadmium (Cd²⁺ and Pb²⁺) are the toxic pollutants. The contamination of these substances in the environment can cause the disorder of organs in human (*e.g.* kidneys, liver, central nervous system, bone). [15-16]

In this study, we aim to develop the high surface area fiber modified electrode based on electrospun G/PANI for the sensitive determination of DA and heavy metals.

2 EXPERIMENT

2.1 Reagents and materials

Graphene (G) nanopowders were obtained from SkySpring Nanomaterials Inc (Houston, TX, USA). Polyaniline emeraldine base (Mw \square 65,000), (+)-camphor-10-sulfonic acid (CSA), polystyrene (Mw \square 180,000), potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium ferrocyanide ($K_4[Fe(CN)_6]$) and potassium chloride (KCl) were purchased from PFCL, Ltd. (New Deli, India). Acetic acid (CH_3COOH), sodium acetate (CH_3COONa), chloroform ($CHCl_3$), dichloromeane (DCM), N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Carlo Erba reagent (Milano, Italy). Dopamine (DA) and ascorbic acid (AA) were purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan). The solutions of Bi^{3+} , Cd^{2+} and Pb^{2+} were diluted from their respective 1000 mgL^{-1} standard solution purchased from VWR International Ltd. (Poole, England). All aqueous solutions were prepared in Mili-Q water (12.8 $M\Omega$ cm).

2.2 Apparatus

An in-house electrospinning system was set up in horizontally for electrode modification. A JSM-6400 field emission scanning electron microscope and a JSM-2100 transmission electron microscope were used for electrode morphology characterization. All electrochemical measurements were preformed on a μ AUTOLAB type III potentiostat controlled with General Purpose Electrochemical System (GPES) software.

2.3 Preparation of screen-printed carbon electrodes

The screen-printed electrodes were prepared using an in-house screen-printing technique. First, the silver/silver chloride ink was screened on polyvinyl chloride (PVC) substrate as the conductive pads. Second, the carbon ink was screened on the same PVC substrate and then, the electrodes were dried in an oven at 55 $^{\circ}C$ about 1 h.

2.4 Electrospinning of G/PANI/PS modified carbon electrode

The G/PANI/PS composite solution containing 2.0 mg of G nanopowders was dispersed in 1 mL of DMF and sonicated for 24 h. PANI emeraldine base 0.40 g was doped with CSA 0.52 g and dissolved in 15 mL of $CHCl_3$. PANI solution was stirred at 1000 rpm for 6 h and filtered. PS solution was prepared in DCM/DMF or in THF/DMF. After that, G, PANI, and PS solution were mixed together. The electrospinning voltage was 10.5 kV, the flow rate was 0.5 mL/h and tip-to collector distance was 15 cm. The electrospun fibers were collected on the screen-printed carbon electrode.

2.5 Electrochemical measurement

A three electrode system was used. The auxiliary electrode was a Pt wire, the reference electrode was an Ag/AgCl electrode and a G/PANI/PS electrospun fibers was used as a working electrode. The electrochemical characterization of the electrospun fibers was measured by cyclic voltammetry (CV) using 1mM $[Fe(CN)_6]^{3-/4-}$ in KCl. Square wave voltammetry (SWV) measurements were performed over a potential range from +0.2 V to +1.8 V with a pulse amplitude of 15 mV, square wave frequency of 30 Hz and step height of 5 mV for DA determination. Anodic stripping voltammetry was employed for the determination of Pb^{2+} and Cd^{2+} .

3 RESULTS AND DISCUSSIONS

3.1 Electrospun G/PANI/PS nanofiber modified electrode for the sensitive determination of dopamine

Prior to electrospinning fabrication, a homogeneous nanocomposite solution containing G, PANI and PS was freshly prepared. Several factors affecting the performance of these modified electrodes were investigated. Among all the parameters, the percentage of G loading (%G) was the main factors that exhibit a profound influence upon the electrochemical response as shown in Figure 1. Based on these results, 6% v/v of G loading was selected for further experiments.

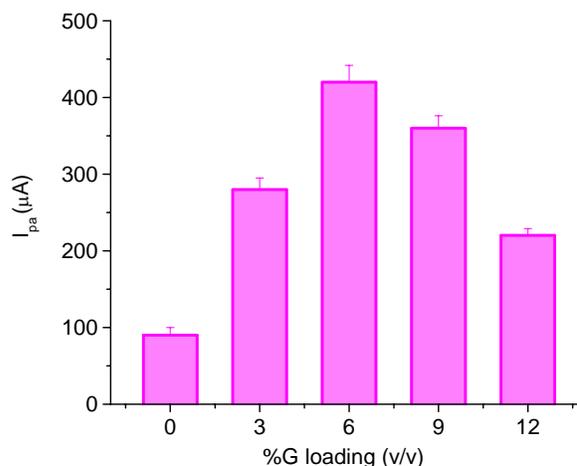


Figure 1. Anodic peak current (i_{pa}) obtained from the cyclic voltammetry of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl using G/PANI/PS nanofiber-modified electrodes with different %G loadings.

The morphology of the electrospun G/PANI/PS nanofibers was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images (Figures 2a-2b) indicate a relatively uniform size distribution and continuous

alignment for the G/PANI/PS nanofibers. Moreover, the TEM images (Figures 2c-2d) confirmed that the G was randomly dispersed inside the nanofibers without any severe aggregation.

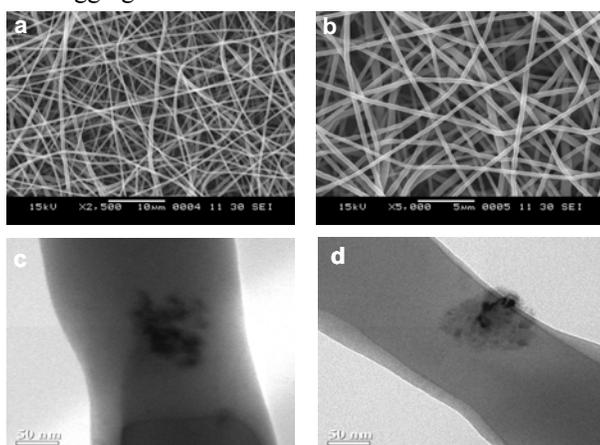


Figure 2. SEM images of the G/PANI/PS nanofibers with 2500× magnification (a) and 5000× magnification (b), and TEM images of random G distributions in the G/PANI/PS nanofibers (c, d).

The electrochemical characteristics of the newly developed G/PANI/PS nanofiber-modified screen-printed carbon electrodes were investigated by CV using a standard $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple. As shown in Figure 3, The G/PANI/PS nanofiber-modified electrodes (red) yielded the highest current response, which was approximately 9 times greater than the unmodified carbon electrode (black). These results verify that the G/PANI/PS nanofibers can facilitate the electron transfer process and thus significantly enhance the electrochemical sensitivity of the modified electrode.

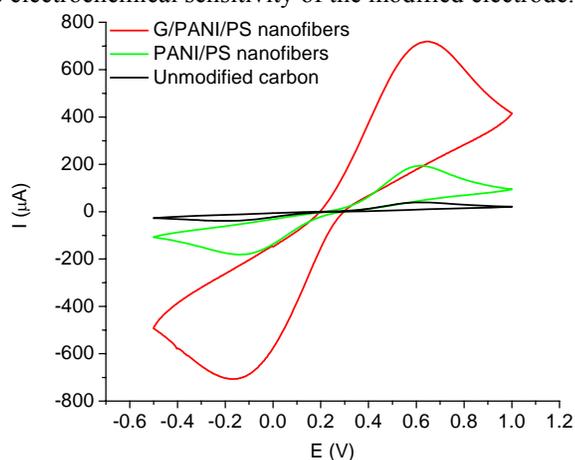


Figure 3. Cyclic voltammograms of 1.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl with the unmodified screen-printed carbon electrode (black), PANI/PS nanofibers modified carbon electrode (green) and G/PANI/PS nanofibers modified carbon electrode with a 6% G loading (red).

The high electrochemical sensitivity of G/PANI/PS modified electrode makes it very attractive for the sensitive determination of DA. A major challenge encountered with DA detection is the interference from AA. As shown in Figure 4a, square wave voltammograms (SWV) of the individual solution of 40 μM DA (black) and 40 μM AA (red) in 0.1 M PBS (pH 7.4) analyzed on an unmodified screen-printed carbon electrode overlapped completely. The ability to selectively determine DA using the G/PANI/PS nanofiber-modified electrode at the highest anticipated concentration of AA was studied. In Figure 4b, the individual voltammograms for 40 μM DA (black) and 40 μM AA (red) in 0.1 M PBS (pH 7.4) analyzed on the G/PANI/PS nanofiber-modified electrode reveals that the anodic peak current of AA (red line) is separated completely from the anodic peak current of DA (black line). Moreover, SWV of a mixture solution (green line) shows the well separation of the peaks of these two compounds. The linear range was found to be 0.0001-100 μM with R^2 of 0.9905. The LOD and LOQ for the system evaluated using signal-to-noise ratios of three ($S/N=3$) and ten ($S/N=10$) were found to be 0.05 nM and 0.30 nM.

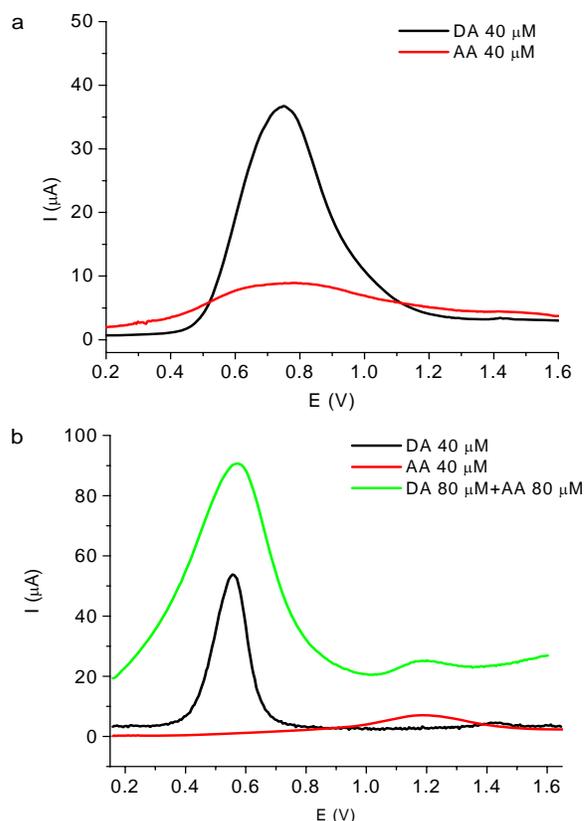


Figure 4. SWV of 40 μM of DA in 0.1 M PBS (black) and 40 μM of AA in 0.1 M PBS (red) analyzed on an unmodified screen-printed carbon electrode (a), and the square wave voltammogram of 40 μM of DA in 0.1 M PBS (black) and 40 μM of AA in 0.1 M PBS (red) and a 80 μM mixture of both DA and AA in 0.1 M PBS (green) analyzed on a G/PANI/PS nanofiber-modified carbon electrode.

3.2 Electrospun G/PANI/PS nanoporous fiber modified electrode for the simultaneous determination of heavy metals

The ratio of organic solvent is one of the most important factors affecting the fiber morphology as shown in Figure 5. The roughness of fibers increases when the percentage of THF increases. At the highest percentage of THF (5d), the uniform porous on fibers is generated, which indicate the greatest surface area fibers compared to the others. This is probably cause by the lower boiling point of THF (66 °C) compared to DMF (153 °C).

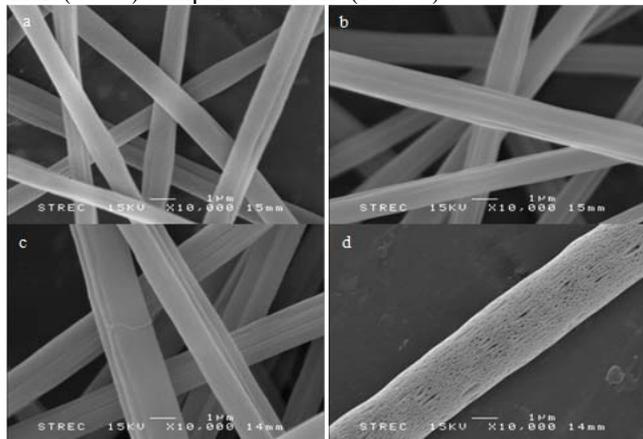


Figure 5. SEM of electrospun fibers of G/PANI/PS from different solvent system (a) 25/75 % THF/DMF; (b) 50/50 % THF/DMF; (c) 75/25 % THF/DMF; (d) 100 % THF).

The G/PANI/PS electrospun modified carbon electrode was applied for the determination of lead (Pb^{2+}) and cadmium (Cd^{2+}) by using anodic stripping voltametry. As shown in Figure 6, both Pb^{2+} and Cd^{2+} are sensitively and simultaneously detected on the porous G/PANI/PS fiber modified carbon electrode; however, Pb^{2+} is undetectable on an unmodified screen printed carbon electrode.

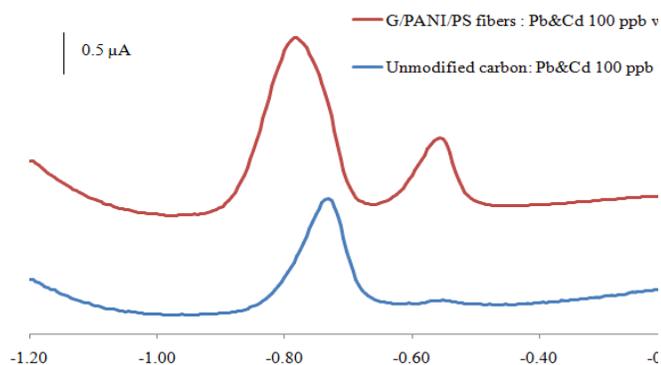


Figure 6. Anodic stripping voltammogram of Pb^{2+} and Cd^{2+} 100 ppb with Bi^{3+} 2.5 ppm in acetate buffer 0.1 M pH 4.5. Potential range of -1.2 and -0.2 V, step height of 4.95 mV, deposition potential of -1.2 V, deposition time of 120 s, amplitude of 10 mV, and frequency of 10 Hz.

4 CONCLUSIONS

Electrospun G/PANI/PS nanofibers and nanoporous fibers were successfully prepared and used for the sensitive determination of dopamine and heavy metals. A very low LOD: 0.05 nM and LOQ: 0.30 nM with a wide dynamic range of 0.1 nM to 100 μ M were achieved for dopamine. The nanoporous fiber was successfully applied for sensitive and simultaneous determination of Cd^{2+} and Pb^{2+} (100 ppb). Eventually, this system was successfully applied to determine dopamine and heavy metals in real samples with excellent reproducibility.

5 ACKNOWLEDGEMENT

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