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ARTICLE

Electrochemical Sensor for Ascorbic Acid Based on Graphene-Polyaniline Nanocomposites

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ABSTRACT

In this study, an electrochemical ascorbic acid sensor was constructed based on a glassy carbon electrode modified with graphene/polyaniline (GN/PANI) nanocomposites. The UV-visible spectroscopy was used to characterize the nanocomposites. Cyclic voltammetry were used to evaluate the electrocatalytic activity towards the oxidation of ascorbic acid in neutral media. The results show that the GN/PANI nanocomposites show excellent electrocatalytic activity toward ascorbic acid oxidation.

KEYWORDS

Graphene, Polyaniline, Ascorbic acid, Electrochemical sensor.

INTRODUCTION

Ascorbic acid (AA, vitamin C), which is a water soluble vitamin, widely present in both the animal and plant kingdoms. Ascorbic acid is commonly used to supplement inadequate dietary intake, as antioxidant and plays an important role in the human metabolism as a free-radical scavenger, which may help to prevent radical induced diseases such as cancer and Parkinson's disease [1]. Furthermore, the deficiency of ascorbic acid can cause scurvy disease. It is administered in the treatment of many disorders, including Alzheimer's disease, atherosclerosis, cancer, infertility and in some clinical manifestations of HIV infections [2]. Thus, the development of a simple and rapid method for the determination of ascorbic acid is desirable for diagnostic and food safety applications. Diverse analytical methods have been developed and used for the detection of ascorbic acid including fluorescence [3], chromatography [4], electrophoresis [5] and electrochemical methods [6,7]. Among these techniques, electrochemical methods have attracted considerable attention due to the advantages of simplicity, low cost, high sensitivity, rapid analysis, easy operation, *etc*.

In order to enhance the sensitivity and selectivity of the electrochemical aptasensors, a variety of materials have been employed to modify electrode. Graphene (GN) is a two-dimensional layer of sp^2 bonded carbon atoms closely packed into a honeycomb lattice [8]. Due to its unique properties such as high surface area, high electrical conductivity and strong mechanical strength, graphene has been widely employed for various applications such as supercapacitors [9], nanoelectronics [10], sensor [11], batteries [12]. However, graphene generally tend to form irreversible agglomerates or even restack to form graphite through strong π-π stacking interaction. This problem has been initially resolved through large-scale production of graphene in the presence of a broad variety of protective reagents, including polystyrene [13], poly(sodium 4-styrene-sulfonate) [14] and didodecyldimethyl-ammonium bromide [15]. However, in most of the cases, the presence of dispersing agents in graphene composite may be undesirable for many techno-logical applications, which usually lead to poor performance [16].

Polyaniline (PANI) is one of the most widely studied conducting polymers. It is highly conductive, exhibits good environmental stability and can easily be prepared. Polyaniline can acts as a suitable matrix for immobilization of biomolecules and mediator for redox and enzymatic reactions and it exhibits impressive signal amplification and antifouling properties [17]. And also, polyaniline is environmentally friendly, water-soluble and can improve the solubility and stability of functional materials. If graphene are modified with polyaniline, it is possible to obtain new materials simultaneously possessing the unique properties of graphene (large surface area) and polyaniline (high conductivity) through combining their individual characteristics, which will provide good opportunities for applications in the fields of sensors, electrocatalysis, luminescence and electronics, *etc*. [18].

In this work, graphene/polyaniline (GN/PANI) nanocomposites were prepared by liquid-liquid interface polymerization method. The prepared nanocomposites were characterized by UV-visible spectroscopy. Cyclic voltammetry was employed to investigate the electrochemical behaviours of ascorbic acid. The nanocomposites show excellent electrochemical oxidation activity toward ascorbic acid. That may be due to the combination of graphene with polyaniline could improve the conductivity, stability and the performance of electrochemical sensors for determination of ascorbic acid. The nanocomposites could be used as a platform for biosensor and biocatalyst applications.

EXPERIMENTAL

Graphite flake (99.8 %, 325 mesh) was provided by Alfa Aesar. Other reagents were of analytical grade and used without further purification. Aniline was fresh distillation prior to use. PBS (0.1 M, pH 7.4) consisting of KH_2PO_4 and Na_2HPO_4 was employed as the supporting electrolyte for detection of ascorbic acid. All aqueous solutions were prepared with doubly distilled water.

Preparation of GN/PANI nanocomposites: The GN/PANI nanocomposites were prepared by reported method [18].

Electrochemical measurement: Electrochemical measurements were carried out on CHI660D electrochemical work station (ChenHua Instruments Co., Shanghai, China). The glassy carbon electrode (GCE, 3 mm in diameter) was polished carefully with alumina slurry (1.0, 0.3 and 0.05 μm) and rinsed with distilled water followed by sonication in nitric acid (1:1), ethanol and distilled water, then dried in a stream of nitrogen gas. A conventional three-electrode system was used, including an Ag/AgCl reference electrode, a Pt wire counter-electrode and the modified electrode as the working electrode. The 6.0 μL of 1.0 mg/mL GN/PANI nanocomposites were carefully cast on the surface of the well-polished glassy carbon electrode and dried in air. And then, the modified electrode was used as the working electrode for all electrochemical studies.

RESULTS AND DISCUSSION

Characterization of GN/PANI nanocomposites: The effective growth of polyaniline on the surface of graphene is characterized by UV/visible spectra. The GN/PANI nanocomposites exhibit three absorbance peaks at λ = 268, 333 and 631 nm (Fig. 1), which can be attributed to the characteristic absorption peak of graphene, the π-π* transition of the benzenoid rings of polyaniline and the π-polaron transition, respectively [18].

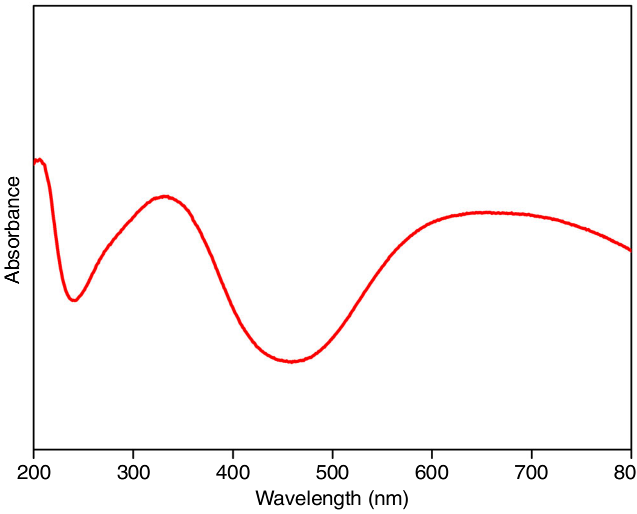

Fig.1. UV/visible spectra of GN/PANI nanocomposites

Electrocatalytic oxidation of ascorbic acid: The electrocatalytic activity of GN/PANI modified glassy carbon electrode towards ascorbic acid was investigated and results are shown in Fig. 2. In the absence of ascorbic acid (curve a), no oxidation peak current change was observed over the potential range employed. After addition of different concentrations of ascorbic acid from 0.74 to 12.7 mM, as shown in curve b to f, the oxidation peak current increases with increasing ascorbic acid concentration. The oxidation peak corresponds to the oxidation of hydroxyl groups to carbonyl groups in furan ring of ascorbic acid on GN/PANI/GCE. Because ascorbic acid at pH 7.0 is negatively charged ($pK_{a,\ ascorbic\ acid} = 4.1$), the enhanced electron transfer kinetics at the GN/PANI/GCE may be due to the formation of hydrogen bonds between the ascorbate and graphene layers in GN/PANI films. The results show that the GN/PANI nanocomposites can catalyst the oxidation of ascorbic acid and the GN/PANI modified glassy carbon electrode has good electrocatalytic activity toward ascorbic acid oxidation. This may be due to the combination of graphene with polyaniline could improve the conductivity, stability and the performance of electrochemical sensors for determination of ascorbic acid.

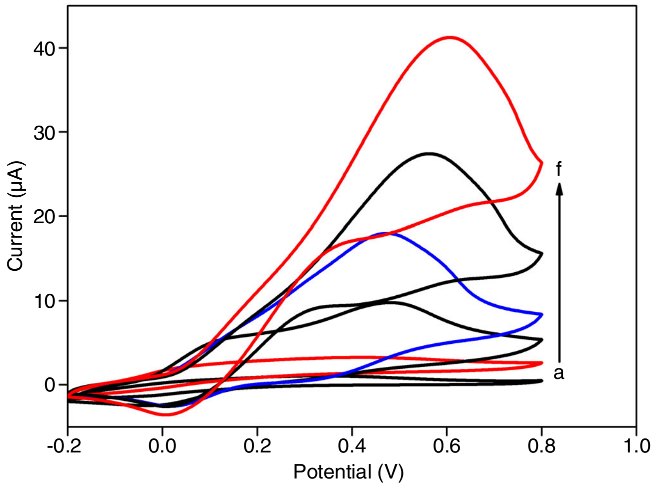

Fig. 2. Cyclic voltammetry curves of GN/PANI/GCE in 0.1 M PBS pH 7.0 without ascorbic acid (a) and with 0.74 mM (b), 1.94 mM (c), 4.5 mM (d), 7.4 mM (e) and 12.7 mM (f) ascorbic acid at a scan rate of 20 mV/s

Conclusion

We have successfully prepared GN/PANI nanocomposites by liquid-liquid interface polymerization method and applied it for constructing an ascorbic acid sensor. GN/PANI nanocomposite provides a large surface area and a high conductivity. The nanocomposite shows an excellent electrocatalytic activity toward ascorbic acid. The results indicate that the graphene and polyaniline can promote the electron transfer of ascorbic acid at the electrode and also improve the conductivity and stability. This sensor platform combines easy fabrication and excellent electrocatalytic activity toward ascorbic acid, which has great potential for sensor applications of several analytes in clinical diagnosis, pharmaceutical analysis and bioelectrochemistry.

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