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Highly Sensitive and Selective Dopamine Biosensor Fabricated with Silanized Graphene

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A new type of chemically modified graphene, EDTA-modified reduced graphene (EDTA-RG), was synthesized by silanization of graphene with N-(trimethoxysilylpropyl) ethylenediamine triacetic acid (EDTA-silane). It was found that the presence of EDTA on the graphene surface enables the formation of a very stable suspension of EDTA-RG in Nafion/ethanol solution. When deposited onto a glass carbon electrode surface, a very stable, uniform thin film of EDTA-RG–Nafion composite was successfully obtained. The electrochemical behavior of this EDTA-RG–Nafion modified electrode, electrochemical catalysis, ionic selectivity, and biocompatibility, have been investigated using a variety of electrochemical techniques. The ion selectivity was investigated by using a negatively charged probe [Fe(CN)₆]³⁻⁻, a positively charged probe, Ru(bpy)₃²⁺, and two biomolecules, dopamine and ascorbic acid. The thin film of EDTA-RG–Nafion composite exhibits high ion selectivity. Performances of EDTA–graphene–Nafion modified electrodes toward dopamine were then evaluated. It was found that the chemical modification process introduces carboxylic groups on the edges of graphene and these functional groups, combined with Nafion, provide an appropriate environment for oxidation of dopamine. The oxidation behavior of dopamine shows excellent reversibility in cyclic voltammetry, which was significantly better than that observed at bare GC, Nafion, and Nafion–graphene coated electrodes. In addition, through the combination of the ionic selectivity of sulfuric from Nafion and EDTA groups in graphene, the EDTA-RG–Nafion film can entirely eliminate the interference from the presence of 1000 times ascorbic acid. The new device is an ideal candidate device for the detection of dopamine.

Introduction

Since their discovery,¹ graphene and its derivatives have attracted much research interest as novel materials with excellent electrical conductivity, mechanical strength, and chemical stability.² Like carbon nanotubes (CNTs), which have been widely used for the study of electrode materials, graphene provides a new avenue for fabricating electrochemical devices because it can facilitate electron transfer between electroactive species and electrodes. Graphene oxides (GO) have been intensively employed as modification materials on the surface of glassy carbon and graphite electrodes. Recently, several studies have reported the construction of electrochemical biosensors using graphene oxide.³–⁵ The graphene-modified electrodes have shown applications in the detection of dopamine (DA), glucose, dihydronicotinamide adenine dinucleotide (NADH), hydrogen peroxide, amino acids, and ascorbic acid (AA).⁶–⁹

Dopamine (DA) is one of many important catecholamine neurotransmitters in the central nervous system of mammals,¹⁰–¹⁴ and dopamine biochemistry is believed to be related to several diseases, such as schizophrenia and Parkinsonism.¹⁵–¹⁸ Therefore, understanding its electrochemical properties and quantifying its presence in human body fluids is most important. DA can be easily oxidized electrochemically at conventional electrodes, which have been used to detect the neurotransmitter both in vitro and in vivo.¹⁹–²¹ However, due to the irreversibility of DA’s electrochemistry, as well as the fouling of the electrode surface by the oxidation products, using conventional electrodes to detect DA generally gives poor results. Also, ascorbic acid (AA) and uric acid (UA) exist in human body fluids at high concentrations and both can be easily oxidized at potentials close to that of DA; thus, their presence interferes with the determination of DA. Furthermore, the concentration of dopamine in the extracellular fluid of the caudate nucleus is extremely low (0.01–1 µM) for a healthy individual and even lower, in the nanomolar (nM) range, in patients with Parkinson’s disease, whereas the concentration of ascorbic acid is 2–3 orders of magnitude higher. Therefore, improving the sensitivity and selectivity of working electrodes toward DA has been a goal of researchers in this area. To meet this challenge, a variety of modified electrodes have been proposed. These include self-assembled monolayer (SAM) electrodes,²²–²⁵ polymer electrodes,²⁶,²⁷ and nanomaterial film electrodes.²⁸,²⁹ Several groups have reported efforts in utilizing various negatively charged polymer films to modify electrodes to determine positively charged DA and to eliminate the interference of AA.³⁰–³² Nanomaterials are widely used because they can provide more active sites and are easier to fabricate. A carbon nanotube is an ideal material because it can be easily deposited onto the electrode surface by covalent linkage, physical absorption, and polymer composites.³³–³⁸ In addition, it can provide catalysis sites for the oxidation of DA.³⁹,⁴⁰ A Nafion cation-exchange polymer is often employed to hold catalytic nanomaterials and other nanomaterials to form composites used to fabricate modified electrodes.⁴¹–⁴³ Nafion itself also acts as a modifier to attract positively charged DA molecules while precluding negatively charged acetate ions.
With a fast response time and higher sensitivity, graphene has shown good prospects as a potential electrode material for detecting DA and other biomolecules. However, the bare graphene, like glass carbon (GC) CNT electrodes, still suffers interference from AA and other biomolecules, such as UA. The combination of reduced graphene (RG) with Nafion has shown some promise as it greatly increases the sensitivity and selectivity of DA detection over AA. However, the problem is that the thicker Nafion films result in lower diffusion rates and thus slower response times. Up to now, there have had no reports about the application of silane-modified graphene for the fabrication of electrochemical devices.

This report presents a synthesized silane-modified graphene and demonstrates its potential applications for fabricating an electrochemical device with Nafion. A silane-modified new graphene derivative was synthesized by utilizing a silanization process to link EDTA functional groups (N-(trimethoxysilylpropyl) ethylenediamine triacetic acid sodium salt) to the graphene surface. It was observed that this silanized graphene shows excellent solubility in aqueous solution and very good conductivity. It was found that Nafion and EDTA—graphene together can form a stable dispersed uniform film on the GC surface. The presence of EDTA functional groups on graphene not only provides active catalytic environments for oxidation of DA but also acts as a barrier to prevent AA from interfering in the detection of DA. The electrochemical determination of DA was performed without any interference from a two-magnitude higher concentration of AA. It was found that the modified electrode has clear advantages over conventional electrodes with excellent reproducibility, good stability, rapid response, and a very low detection limit of 0.01 µM.

Experimental Section

Equipment. The electrochemical tests were performed on a CHI-660 electrochemical workstation (CHI Instruments Co., Texas) with a three-electrode system, with a GC electrode as the working electrode, the saturated calomel electrode (SCE) as a reference electrode, and a Pt wire as a counter electrode. The film morphologies were investigated with a Philips XL-30 ESEM scanning electron microscope (SEM).

Materials. Graphene oxide and reduced graphene oxide were prepared in our lab with the Hummers method and purified and reduced. Their sizes were several hundred nanometers to several micrometers, respectively, based on the starting graphite and treatment procedures. N-(trimethoxysilylpropyl) ethylenediamine triacetic acid sodium salt, 45% in water (Gelest Inc.), was used as the silane functionalization agent. Nafion, dopamine, and ascorbic acid tris(bipyridine) ruthenium(II) (Ru(bpy)32+) chloride were ordered from Sigma. All of other reagents and solvents were used without further purification.

Silanization of Graphene. To silanize graphene oxide, 10.0 mg of GO was added into a three-neck flask with 50.0 mL of ethanol and dispersed through ultrasonication (in a water bath) for 60 min. A 1 mL portion of a 1.0 wt % hexane solution of N-(trimethoxysilylpropyl) ethylenediamine triacetic acid sodium salt was then added and stirred for 12 h at 60–65 °C for silanization. After the reaction finished, 100 mL of methanol was added to dilute the unreacted silane solution. The product was obtained by filtration and washing sequentially with methanol, water, and acetone. The silane-treated GO was dried in a vacuum oven at 80 °C for 12 h and then dispersed into 50 mL of DI water and reduced with hydrazine. Upon being reduced, the color of the solution changed from brown to black. Chemical structures of graphene and EDTA-modified graphene are shown in Figure 1.

Electrode Preparation. To deposit a Nafion—graphene film on an electrode surface, a 3 mm GC electrode (CHI instruments) was sequentially polished with 1, 0.3, and 0.05 µm alumina powder and then washed ultrasonically in water for a few minutes and then in ethanol for a few minutes. The cleaned GC electrode was dried in a nitrogen steam. The RG—Nafion and EDTA-RG—Nafion coated GC electrodes were prepared by casting 2.5 µL of an RG—Nafion or EDTA-RG—Nafion suspension (0.1–1 mg mL−1) on the GC surface and drying at room temperature. The as-prepared electrodes are named GC electrode, Nafion/GC electrode (Nafion-coated GC electrode), RG/Nafion/GC electrode (Nafion—reduced graphene composite coated GC electrode), and EDTA-RG/Nafion/GC electrode (EDTA-modified reduced graphene Nafion coated GC electrode), respectively. Before electrochemical testing, Nafion/GC, RG/Nafion/GC, and EDTA-RG/Nafion/GC electrodes were all immersed in DI water or pH 7.2 phosphate buffer solution (PBS) for 1 h. After the test and when not in use, the electrodes were stored in PBS solution at 4 °C.

Solubility of EDTA—Graphene and Its Compatibility with Nafion. From our previous report, the EDTA-modified graphene exhibits graphene solubility in aqueous solution (Figure 2a). It was found that a very stable suspension of EDTA-RG—Nafion solution can be prepared by mixing EDTA-RG directly into 0.5% Nafion solution. Compared with an RG—Nafion suspension, a well-dispersed EDTA—graphene suspension is formed in Nafion solution (Figure 2b). Precipitation was observed of the RG—Nafion suspension after 24 h; however, the suspension of EDTA-RG—Nafion is very stable over several months. By depositing 2.5µL of the above solution onto a GC electrode, a very stable film can be formed on the GC surface, and this film
firmly and uniformly attaches onto a glassy carbon electrode (Figure 2d). As a control sample, dried EDTA-RG without Nafion is depicted in Figure 2c. This is caused by the high dispersity of the EDTA-RG-Nafion solution because of the relatively low surface energy and high surface-to-volume ratio of EDTA-RG. Individual graphene sheets can disperse into Nafion solution very well.56 Once deposited on the GC surface, EDTA-RG tends to form a uniform film on the GC surface. The uniform surface, along with the high conductivity of RG, provides a favorable environment for electrochemical tests of biomolecules, such as DA.

Results and Discussion

Ionic Selectivity of EDTA/RG/Nafion Film. The voltammetric response toward AA in pH 7.2 solution was measured for four electrodes: GC, Nafion/GC, RG/Nafion/GC, and EDTA-RG/Nafion/GC electrodes. Figure 3 depicts the results of cyclic voltammetric (CV) responses of AA at the four electrodes. An oxidation peak at 0.18 V appeared at a bare GC electrode (Figure 3a). This is in contrast to the oxidation curve without an obvious peak observed at the Nafion-coated electrode (Figure 3b). These data are in accordance with others’ results41–43 where it has been stated that, in a Nafion-coated electrode system, the sulfuric group of Nafion is a barrier for AA because the Nafion layer can prevent the diffusion of AA into the film. The same phenomenon was observed at an RG/Nafion/GC electrode. Figure 3c illustrates the CV responses of AA at an RG/Nafion/GC electrode, in which an oxidation curve of AA without an obvious peak was observed, but with a higher response current. The increased oxidation current is due to the increase in electrode active surface area provided by RG. In this work, the thinner layer of Nafion, fabricated by 2.5 µL of a 0.1% RG/Nafion suspension onto a φ = 3 mm GC electrode, cannot completely block the diffusion of AA and hence cannot prevent AA from interfering with the detection DA. To totally block the diffusion of AA, a thicker Nafion film is necessary. However, a thicker Nafion film will lower the diffusion rate, increase the background currents, decrease the sensitivity, and prolong the response time. Fortunately, this problem was overcome by using the EDTA-RG/Nafion/GC electrode. No voltammetric response of AA was observed at an EDTA-RG/Nafion/GC electrode (Figure 3d). The observed cyclic voltammetric responses of AA at an EDTA-RG/Nafion/GC electrode is the same as that in blank solution without AA, indicating that the EDTA-RG/Nafion/GC film can block the diffusion of AA into the electrode surface. In addition, the large background current is attributable to the increase of the electrochemically active surface.57,58

To further investigate the extent of the effects of a negative charge on the graphene surface, a cyclic voltammetric study for the above four electrodes was performed utilizing a negatively charged redox probe, [Fe(CN)₆]³⁻/⁴⁻, and a positively

Figure 2. (a) Photograph of suspensions of RG and EDTA-RG in water after 4 weeks. (b) Photograph of suspensions of RG/Nafion and EDTA-RG/Nafion after 4 weeks. (c) SEM image of EDTA-RG. (d) SEM image of EDTA-RG/Nafion film formed on the GC surface.

Figure 3. Cyclic voltammograms of bare GC (a), Nafion/GC (b), RG/Nafion/GC (c), and EDTA-RG/Nafion/GC (d) electrodes in blank PBS (pH = 7.2) (black) and PBS with 10 mM ascorbic acid (red). Scan rate 60 mV/S.
charged redox probe, Ru(bpy)$_3^{2+}$. It was expected that the electron-transfer reaction involving [Fe(CN)$_6^{3-}$] at a negatively charged electrode surface will be blocked by the repulsive electrostatic forces. Figure 4a supports this expectation. The responses of 5.0 mM [Fe(CN)$_6^{3-}$/4$^-$$]$ in 0.2 M Na$_2$SO$_4$ at both Nafion/GC and EDTA-RG/Nafion/GC electrodes are diminished compared with that at the bare GC electrode. The voltammogram obtained from the GC electrode exhibited a redox peak pair with a $\Delta E_p$ value of about 69 mV, but the voltammogram obtained at the EDTA-RG/Nafion/GC electrode only exhibited a redox curve with no obvious peak and with a peak current one magnitude smaller than that of the GC surface. Contrary to the negatively charged redox probe [Fe(CN)$_6^{3-}$/4$^-$$]$, it is expected that the electron-transfer reaction involving Ru(bpy)$_3^{2+}$ at the negatively charged electrode surface would be enhanced because of the attractive electrostatic forces. This indeed was confirmed in Figure 4b. The response of 1.0 mM Ru(bpy)$_3^{2+}$ in 0.2 M Na$_2$SO$_4$ at both Nafion/GC and EDTA-RG/Nafion/GC electrodes is increased 4- to 8-fold compared with that at the bare GC electrode, respectively. These observations proved that the presence of negative charges on graphene repels the negatively charged [Fe(CN)$_6^{3-}$/4$^-$$]$ ions, thereby resulting in a 1 order of magnitude lower peak current density. On the contrary, the EDTA-RG/Nafion/GC electrode attracts the positively charged Ru(bpy)$_3^{2+}$ and resulted in a 1 order of magnitude increase of the peak current. These results exhibit the ionic-selectivity properties of EDTA-RG and predict its potential applications as ion-selective electrodes.

**Response to Dopamine.** Cyclic voltammetry of DA in the presence of AA was then investigated. At pH 7.2 PBS, with the presence of 10 mM AA, the cyclic voltammograms of 10.00 $\mu$M DA at GC, Nafion/GC, RG/Nafion/GC, and EDTA-RG/Nafion/GC electrodes are shown in Figure 5a. A broad, ill-defined redox wave of the DA and AA mixture was observed at the bare GC electrode with an oxidation peak ($E_{pa}$) at 0.410 V and a reduction peak ($E_{pc}$) at 0.010 V. At Nafion/GC, the oxidation peak ($E_{pa}$) was observed at 0.348 V and reduction peak ($E_{pc}$) at 0.082 V. At the RG/Nafion/GC electrode, the $E_{pa}$ of DA is 0.298 V and $E_{pc}$ appeared at 0.087 V. At the EDTA-RG/Nafion/GC electrode, the $E_{pa}$ of DA is 0.199 V and $E_{pc}$ appeared at 0.119 V. The increase in oxidation currents of DA at Nafion/GC and RG/Nafion/GC electrodes is the result of two factors: first, the presence of RG and EDTA-RG significantly enhances the active electrode surface area and, second, a concentration of DA from the solution through the anionic sulfuric groups of Nafion structures and the carboxylic groups at the RG surface, which occurs upon immersing the electrode into the DA solution. Nafion can enhance the sensitivity of the bare GC electrode for DA and has the adverse effect of a large resistance to the diffusion of DA. Nafion itself not only acts as an anion barrier but also acts as a concentrated functional film in this electrode system. This study demonstrates that thicker Nafion film will result in a higher selectivity but will lower the mass transfer rate of DA and the sensitivity, whereas thinner film results in the poor selectivity of DA. Figure 5b depicts the responses of the EDTA-RG/Nafion/GC electrode to a blank solution, AA solution, and AA$^+$DA solution. It is clear that no response current was observed at the EDTA-RG/Nafion/GC electrode with the presence of AA only. Upon the addition of DA to the AA solution, a pair of
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TABLE 1: Electrochemical Parameters of AA and DA at Four Types of Electrodes

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Ascorbic Acid (10 mM)</th>
<th>Dopamine (10 mM)</th>
<th>AA (10 mM)</th>
<th>DA (10 mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pa} (V)^a$</td>
<td>$I_{pa} (\mu A)^a$</td>
<td>$E_{pc} (V)^b$</td>
<td>$I_{pc} (\mu A)^b$</td>
</tr>
<tr>
<td>GC</td>
<td>0.190</td>
<td>2.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion/GC</td>
<td>none</td>
<td>none</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RG/Nafion/GC</td>
<td>none</td>
<td>none</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDTA-RG/Nafion/GC</td>
<td>none</td>
<td>none</td>
<td></td>
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$dopamine (10.00 \mu M)$

<table>
<thead>
<tr>
<th>Electrode Type</th>
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<tr>
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<td>none</td>
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<tr>
<td>EDTA-RG/Nafion/GC</td>
<td>none</td>
<td>none</td>
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</table>

$^a$ $E_{pa}$, the anodic peak potential; $E_{pc}$, the cathodic peak potential; $I_{pa}$, the anodic peak current; $I_{pc}$, the cathodic peak current. $^b$ None = No peak can be observed.

The cyclic voltammograms of DA at the EDTA-RG/Nafion/GC electrode in PBS (pH 7.2) with 10 mM AA + 10.00 \mu M DA. Scan rates: 20, 40, 60, 80, 100, 150, and 200 mV/S. (b) The relation between peak currents versus the square root of the scan rate. (c) The relation between peak currents versus the scan rate.

Generally, the conductivity of the electrode material and the surface properties, especially the surface active functional groups, determine the electrochemical properties of the electron transfer of reactants. The EDTA-RG electrode offers several advantages compared to other electrodes: high conductivity, large surface area, uniform structure, and biocompatibility. Most importantly, it can accommodate much more active functional groups in a given region by a chemical modification technique. The presence of EDTA-silane provides a suitable environment for the electrocatalysis of DA oxidation. Several active functional groups, such as amino groups, carbonyl groups, and carboxyl groups, can act as media to enhance the electron transfer and catalyze the oxidation of DA at the graphene surface and thus shift the oxidation potentials of DA at the electrode.

The cyclic voltammogram of DA at the EDTA-RG/Nafion/GC electrode exhibited a pair of well-defined redox peaks with $E_{pa} = 0.199 \text{ V}$, $E_{pc} = 0.119 \text{ V}$, and $\Delta E_p = 80 \text{ mV}$. The higher redox currents and negatively shifted oxidation potential demonstrate that EDTA-RG/Nafion film can effectively enhance the oxidation of DA and greatly improve the redox peak shape. The higher oxidation currents are a result of a higher surface area and concentration process. The negative shift of the oxidation potential indicated an enhanced effect of DA at the EDTA-RG/Nafion film. The smaller $\Delta E_p$ of DA at the EDTA-RG/Nafion/GC electrode may be ascribed to the increase in the mass transfer rate of DA in EDTA-RG and Nafion composite film and indicates a uniform structure of the composite film. A possible reason may be conjectured to the uniform structure of EDTA-RG/Nafion film, fabricated though a uniform suspension of EDTA-RG/Nafion (Figure 2d). A well-packed, highly ordered structure film of Nafion–EDTA-RG was formed during the drying process of the EDTA-RG/Nafion suspension mixture. The structural compatibility between EDTA-RG and Nafion facilitates EDTA-RG/Nafion film formation on the GC surface with a uniform structure. These properties can be confirmed by an electrochemical kinetic investigation. Figure 6 depicts cyclic voltammograms of DA at the EDTA-RG/Nafion/GC electrode through the scan range from 20 to 200 mV/S. The relation between redox peak currents and the scan rates predicts a hybrid kinetic process. At lower scan rates (from 20 to 80 mV/S), the electrochemical redox behavior of DA at the EDTA-RG/Nafion/GC electrode surface is a diffusion-controlled process, and the current peak is proportional to the square root of the scan rate. At higher scan rates (>100 mV/s), the relation...

Figure 7. The voltammetric responses of various concentrations of DA at the EDTA-RG/Nafion/GC electrode. Scan rate = 60 mV/S. Concentrations: 0.00, 1.00, 2.00, 3.00, 6.00, 10.00, 15.00, and 25.00 \mu M (with 1 mM AA in pH = 7.2 PBS).
between redox peak currents and the scan rates is linear, implying a surface absorption-controlled process. These phenomena suggest that, at low scan rates, DA can easily diffuse through EDTA-RG/Nafion film, and there is sufficient time for the film to behave as a three-dimensional electrode, with significant contributions from species diffusing within thin layers. On the contrary, at high sweep rates, there is not enough time for diffusion of DA through the EDTA-RG/Nafion film, and therefore, the electrochemical oxidation process is an absorption behavior. It is envisaged that the reaction occurs not only at the outer surface of the electrode but also at reactive sites within the adsorbed assembly.

The above results strongly suggest that the hybrid film of the EDTA-RG/Nafion composite can take all of the advantages from EDTA-graphene and Nafion and contribute to the performance of the electrode as a DA sensor. Sulfuric groups of Nafion and EDTA groups of EDTA-RG not only provide a suitable environment for DA oxidation but also accelerate electron transfer between DA and the electrode significantly, therefore, resulting in a remarkably increased response signal toward the redox of DA in contrast to the bare or RG/Nafion electrode alone. The combination of ion-exchange characters of Nafion and the EDTA groups can also concentrate DA from solution and thus increase the sensitivities of detection. In addition, the combination of sulfuric groups linked to the graphene surface provides a favorite environment for the oxidation of DA with an oxidation peak potential negative shift of DA at the EDTA electrode. The EDTA groups, combined with ionic sulfuric groups of Nafion, can concentrate the DA from solution and thus increase the sensitivities of detection. In addition, the combination of sulfuric groups of Nafion and carboxylic groups of EDTA-RG can totally block the diffusion of ascorbic acid and thus eliminate its interference on the detection of DA. The sensitivity of the sensor along with its improved selectivity might allow for its potential use in the investigation and diagnosis of dopamine-related diseases.

Conclusions

A new type of EDTA chemically modified graphene, EDTA-RG, was synthesized and found that it can be used as an ideal electrode material to fabricate biosensors. A dopamine electrochemical biosensor with a high selectivity had been made by applying EDTA-RG/Nafion film onto a glass carbon electrode. The unique structure of EDTA-RG film offers several advantages over normal reduced graphene. The EDTA-RG in the composite film not only greatly improved the electrochemical activity in physiologically relevant solutions but also increased the effective electrode surface area. The presence of EDTA groups linked to the graphene surface provides a favorable environment for the oxidation of DA with an oxidation peak at 0.14 V.

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References and Notes
