Electrochemical Behavior of Glassy Carbon Electrode Modified by Layer-by-layer Self-assembly of Functional Graphene

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Abstract. In this paper, an electroactive polymer (PEI-Fc) was prepared by bonding ferrocene groups to the backbone of poly(ethyleneimine). On the other hand, sulfo-group modified graphene oxide (SGO) was also prepared. The multilayer film was constructed on glassy carbon electrode surface by the layer-by-layer adsorption method using PEI-Fc, SGO and PSS. The electrochemical activity of ferrocene in PEI-Fc/PSS or PEI-Fc/SGO film modified electrode was studied, especially the influence of layer number and pH. It is shown clearly that the graphene oxide (GO) has an inhibitory effect of electron transfer. Reduction of graphene oxide (RGO) increases the specific surface area of the glassy carbon electrode, and it is an ideal candidate for electrode modification. It is also found that ferrocene exhibited stronger electrochemical response in PEI-Fc/SGO film compared to the film without SGO. And the response of ferrocene increased with layer number and decrease of pH.

1. Introduction
Layer-by-layer (LBL) self-assembly is a versatile method for the fabrication of multilayer films [1]. Different interaction forces are exploited in the LBL self-assembly technique, including the electrostatic force [2], the hydrophobic force [3], hydrogen bonding [4] and covalent bonding [5]. To obtain a LBL deposited multilayer film, the selected substrate is alternately dipped into solutions of inorganic materials and oppositely charged polymers [5]. Because of its simple operation, flexible method, and precise control, the LBL self-assembly technique has been widely used.

Graphene, a relatively new material with a one-dimensional nanostructure, has attracted much attention in diverse scientific fields since its discovery in 2004 [6]. Graphene comprises a single layer of sp\textsuperscript{2}-bonded carbon atoms with a high surface-to-volume ratio, which provides it with unique electrical, thermal and mechanical properties [7]. Currently, many techniques are used to produce high quality graphene, such as micromechanical exfoliation, epitaxial growth, chemical vapor deposition, and the reduction of graphene oxide (GO). However, owing to the strong Van der Waals attraction between the graphene layers, these methods fail to obtain stable single layer sheets. This severely limits its use for fundamental studies and practical production. To overcome this, graphene sheets have been functionalized with hydroxyl (OH) and epoxy groups on the basal plane and carboxylic acid (COOH) groups at the edges. This GO is a single-atomic-layer sheet and prepared by the chemical oxidation and exfoliation of graphite. In contrast to graphene, GO can be stably dispersed in an
aqueous solution without any stabilizing agent [8]. In water, the COOH groups on the edges of GO become negatively charged, which causes the GO sheets to separate and adsorb on the cationic polyelectrolytes. Therefore, GO is a promising material for the preparation of nanocomposites [9].

2. Experimental

2.1. Materials

GO (oxidation degree >95%) in powder form was purchased from Tanfeng Technology in China. Ferrocene-carboxyaldehyde (FcCHO), sodiumborohydride (NaBH4), polyethylenimine (PEI, MW 25,000) were obtained from Sigma (USA). All the other chemicals used were of analytical grade and all solutions were prepared with double distilled water. A conventional three electrode cell was used, the working electrode used was glassy carbon electrode (GCE) or the modified electrode, a platinum electrode was applied as the counter electrode and an Ag/AgCl electrode served as a reference electrode. All potentials in this paper were measured and reported versus Ag/AgCl. The structure of PEI-Fc and single-layer GO are shown in Figure 1.

Fig. 1 (a) Chemical structure of PEI-Fc and (b) Single-layer GO sheet.

2.2. Synthetic procedure

The synthesis of SGO was carried out with a procedure consisting of the synthesis of the arenediazonium salt and its subsequent reaction with the GO. Typically, 1 g of sulfanilic acid (SA), 12 mL of the HCl solution and 0.4 g NaNO2 were successively added into 20 mL of a NaOH solution (2wt. %) under mechanical agitation. The reaction was kept at 0°C for 15 min, which led to the formation of the diazonium salt. The obtained arenediazonium salts was then added into 200 mL of the GO suspension with a concentration of 1 mg·mL⁻¹. After 4 h of stirring in an ice bath, the product was washed with water and centrifuged until the pH value of the solution reached to 7. After a freeze-drying process, the sponge like SGO was obtained. Figure 2 briefly illustrates the procedure for the preparation of SGO.
3. Results and Discussion

For the PEI-Fc/GO system, the film fabrication started with the adsorption of the positively charged PEI-Fc layer with a branched structure onto a pretreated negatively charged GCE substrate. Then, GO sheets functionalized with phenolic OH and COOH groups were adsorbed onto the positively charged PEI-Fc coated surface. The alternating sequential adsorption of PEI-Fc and GO layers resulted in the wall structure of a multilayer film on the GCE substrate.

As shown in the figure 3, FTIR spectroscopy of GO revealed the presence of C-O (νC-O at 1060 cm⁻¹), C-O-C (νC-O-C at 1240 cm⁻¹), C-OH (νC-OH at 1360 cm⁻¹) and C=O, in carboxylic acid and carbonyl moieties (νC=O at 1740 cm⁻¹) which proves the sufficient oxidation of GO. The peaks at 1270, 1117, 1025, and 870 cm⁻¹ were assigned to the asymmetric stretching of O=S=O, symmetric stretching vibration of O=S=O, stretching of S=O, and stretching of S-O of the sulfonic acid group in S-GO, respectively. This suggests that the sulfonic acid group exists on the GO surface. Meanwhile, the peaks at 1740 cm⁻¹, 1360 cm⁻¹, 1240 cm⁻¹, and 1060 cm⁻¹ (carboxyl, hydroxyl, and epoxied) are severely attenuated in SGO, implying a partial reduction of GO.

Fig. 2 Procedure for the preparation of SGO.

Fig. 3 FTIR spectroscopy of GO and SGO
Figure 4 shows that the cyclic voltammograms of bare GCE electrode and GCE electrode modified with GO and RGO at the same scan rates in the potential range between -0.2 and 0.6 V. When cyclic voltammetry was performed using potassium ferricyanide as a probe, one-electron reversible conversion occurred on the surface of the electrode, which was in accordance with Randles-Sevick formula: 

$$I_{pa} = \frac{n^2}{2\pi kF^2} A C_0 D^{1/2} v^{1/2},$$

where $I_{pa}$ is the anodic peak current; $C_0$ is the concentration of potassium ferricyanide solution; $A$ is the actual area of the electrode; $n$ is the electron transfer number; $v$ is the scanning speed; and $D_r$ is the diffusion coefficient. In a potassium ferricyanide solution at a concentration of 2 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl, $n = 1$ and $D_r = 7.6 \times 10^{-6}$ cm$^2$·s$^{-1}$. Some information can be obtained from the formula when the substrate concentration and the same scanning speed, the actual area ratio of two electrodes $A_1/A_2$ is equal to its anodic peak current ratio $I_{ap1}/I_{ap2}$. If the two electrodes in the potassium ferricyanide solution anode peak current and root of scanning speed conform to liner, the actual area ratio of $A_1 / A_2$ is equal to the ratio of the slope of two straight lines. It can be concluded that the actual area of the RGO modified electrode is about 2.8 times the area of the bare electrode, in other words, the surface roughness of the RGO modified electrode is 2.8 times than that of the bare electrode.

Figure 5 shows the cyclic voltammograms of glass carbon electrode modified with two, four and six bilayers of PEI-Fe/SGO (from inner to outer) in 50 mM phosphate buffer (pH 7.4) at a scan rate of 100 mV·s$^{-1}$. 
As shown in the figure 5, a reversible and nearly symmetric redox peak appears at about 0.4 V of glass carbon electrode modified with bilayers of PEI-Fc/SGO, which is not found on the bare electrode in 0.1 mol·L\(^{-1}\)PBS buffer solution (pH = 7.4), proving that this peak resulted from the electrochemical reaction of ferrocene groups in PEI-Fc. At the same time, the redox peak current also increased with the number of layers. It is inferred that the multilayered film is formed on the surface of the electrode and the ferrocene component shows significant electrochemical activity. As shown in the figure 6, when the pH of solution is different, it is found that the modified electrode has the largest electrochemical response at pH = 5.0. The cyclic voltammetry (pH = 5.0, scan speed = 100 mV·s\(^{-1}\)) of the PEI-Fc / SGO film layer increases at the same pH, the oxidation peak current is also significantly increased, indicating that the more ferrocene content, the peak current showed greater. As shown in figure, the cyclic voltammogram of PEI-Fc / SGO at different pH shows a redox peak current increasing as the pH decreases.

![Cyclic voltammograms](image)

**Fig. 6** (a) Cyclic voltammograms of glass carbon electrode modified with two, four and six bilayers of PEI-Fc/SGO (from inner to outer) in 50 mM phosphate buffer (pH =5.0) at a scan rate of 100 mV·s\(^{-1}\); (b) Cyclic voltammograms of glass carbon electrode modified with six bilayers of PEI-Fc/SGO at different pH (pH=5.0,5.8,6.6,7.4) and a scan rate of 100 mV·s\(^{-1}\) in 50 mM phosphate buffer.

4. Conclusion

The functional graphene SGO and the electrochemically active polymer PEI-Fc were obtained and multilayer film modified electrodes containing PEI-Fc and SGO were prepared by the layer-by-layer self-assembly method. The results show that the electrochemical response of ferrocene increases with the number of layers. The electrochemical activity of multilayer PEI-Fc/SGO film modified electrodes at different pH was investigated. The lower pH, the higher redox peak current was obtained. In summary, the graphene modified electrode has good stability and recognition, and the PEI-Fc/SGO film modified electrode prepared in this experiment can better fix the ferrocene on the electrode surface.

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