Abstract
Cobalt phthalocyanine-graphene (CoPc-Gr) complex are fabricated through $\pi-\pi$ interaction of each components, with CoPc adsorbed/inserted on/in the graphene sheets. The obtained complex could be used in the electro-chemical detection of various medicines. CoPc-Gr modified glassy electrode shows excellent response to the electro-oxidation of dopamine (DA) and ascorbic acid (AA), much better than those of CoPc, graphene oxide (GrO) or graphene (Gr) modified electrode. Significantly, the detection of dopamine is a diffusion-controlled process, highly selective, and has a low detection limit and broad linear range.

Key words
cobalt phthalocyanine-graphene; dopamine; electro-oxidation; selective detection

1. Introduction
Dopamine (DA) is a very important neurotransmitter which plays a significant role in the function of the renal, hormonal and central nervous systems [1]. It has a close relationship with not only learning and memory formation but also pathological processes of Parkinsons disease [2]. So in electroanalysis, a low cost, high sensitivity and easy operation method of DA detection is an attractive area [3–5]. Many types of materials have been proposed as electrode materials for accurate determination of DA under the interference of ascorbic acid (AA), coexisting with DA in organisms which shares a similar oxidation potential with DA in electro-chemical oxidation process. Recently, carbon materials, especially graphene and its derivate, have been used in catalytic oxidation reaction as well as electro-chemical oxidation processes [6–12]. Graphene possesses a large $\pi$-electron structure, apt for $\pi$-stacking type adsorption, and its open edges (armchair or zig-zag) also give it an extra electronic state due to a localized state at the edges [13,14]. Therefore, graphene has been considered as an attractive new material for electro-chemical sensors [15–18].

In this work, we organized cobalt phthalocyanine (CoPc), a good electro-catalytically active material [2,19] onto/into graphene sheets through a strong $\pi-\pi$ interaction between CoPc and graphene. And then the composite was applied for electro-oxidation and determination of DA under the interference of AA and it shows significantly improvement in electro-chemical performance compared with graphene, CoPc or graphene oxide (GrO), respectively.

2. Experimental
2.1. Reagents and materials
Graphite flake (nature, 300 mesh) was taken from Liu Mao mine, China. Nafion (5 wt%, Alfa Aesar) was diluted to 0.1 wt% with distilled water. Dopamine hydrochloride was obtained from Alfa Aesar. Other reagents were purchased from Beijing Chemical Company. All the solutions were prepared with deionized water (18.2 MΩ).
2.2. Synthesis of CoPc-Gr

GrO was prepared from graphite powder by a modified Hummers method [20] and graphene (Gr) was prepared by reducing GrO using N\textsubscript{2}H\textsubscript{4} [21]. For preparing CoPc-Gr, 0.5 g CoPc was put into the mixed solvent containing 1 mL trifluoroacetic acid, 0.5 g graphene and 8 mL chloroform and then the mixture was stirred for 2 h after being ultrasonically dispersed for 1 h. The stirring mixture was heated in the oil bath at 333 K until the solvent was evaporated to dry. The powder was washed with a solution (volume ratio: 90\% CH\textsubscript{3}OH, 5\% H\textsubscript{2}O, 5\% NH\textsubscript{3}·H\textsubscript{2}O) and then with ethanol until the filtrate was colorless. The sample was dried at 333 K for 24 h to get CoPc-Gr.

2.3. Characterization

SEM images were collected on a KYKY-AMRAY-1000B microscope. TEM images were obtained with a Tecnai G220 S-Twin microscope operating at an accelerating voltage of 200 kV. XPS spectra were obtained using an Axis Ultra spectrometer (Kratos, UK). A mono Al K\textsubscript{α} (1486.6 eV) X-ray source was used at a power of 225 W (15 kV, 15 mA). To compensate for surface charge effects, binding energies were calibrated using C 1s peak at 284.8 eV. UV-visible spectroscopy was collected on a Cary Varian 50 machine with a 1 cm quartz sample cell. Electro-chemical measurements were conducted using CHI660D electro-chemical workstation (CHI, Shanghai) with three-electrode setup. Glassy carbon electrode (GCE, 3 mm diameter, Tian Jin Aida, Inc.) acted as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum wire as the counter electrode. XRD patterns of the catalysts were recorded using a D/max-rB X-ray diffractometer (Japan) with a Cu K\textsubscript{α} radiation source operating at 45 kV and 100 mA.

2.4. Preparation of modified glassy carbon electrodes

Glassy carbon electrode (GCE) was polished with 70 nm Al\textsubscript{2}O\textsubscript{3} power, rinsed by deionized water, ethanol and deionized water, and dried at room temperature. 5 mg CoPc, GrO, Gr or CoPc-Gr was dispersed in 1 mL of 0.1 wt% nafion solution. A 10 \textmu L aliquot of this dispersion was placed as a droplet on the pre-treated GCE to fabricate the modified GCE. The solvent was evaporated under an infrared lamp.

3. Results and discussion

The prepared CoPc-Gr were first characterized by UV-vis absorption spectroscopy (Figure 1a) with CoPc and graphene as reference. Compared with CoPc, the Q-bands and Soret bands for CoPc-Gr were slightly red shifted to 663 and 600 nm, respectively, indicating a strong \pi−\pi interaction between CoPc and Gr, which leads to the relocation of the electrons from graphene sheets to the phthalocyanine group of CoPc [22]. As shown by Raman spectra in Figure 1(b), CoPc-Gr showed significantly stronger D-band and weaker G-band compared with Gr, indicating that possibly there are more edge-plane defects on the complex [23]. The characteristic peaks of CoPc were also visible on the spectra, which means that CoPc had been absorbed onto/into the graphene sheet. The result was also verified by ICP which showed there was about 14 wt\% CoPc in CoPc-Gr complex. TEM images (Figure 1c and 1d) of CoPc-Gr showed the same film structure as graphene with many wrinkles and SEM image (Figure 1e) showed that CoPc-Gr was composed of several layers of sub-units. EDX results suggested that Co was barely detectable on the surface of the complex stacks but there was around 3 wt\% Co on the cross section of the stacks. We proposed that most of CoPc was trapped between the stacks. However, no apparent small angel shift of the (002) diffraction was observed on XRD patterns of CoPc-Gr as compared with that of Gr (Figure 2a), while the (100) and (101) diffractions of CoPc-Gr are much weaker than those of Gr, indicating the complex interaction mode of the two components [24]. Co 2p XPS spectra of CoPc and CoPc-Gr are shown in Figure 2(b). Significantly, we noticed a 0.4 eV shift on Co 2p\textsubscript{3/2} signal after the introduction of CoPc onto/into Gr (from 780.9 to 780.5 eV). This shift indicates that the electron transfer from Gr to Co ion. The donation of electron and thereby the change of the charge density at the phthalocyanine ring were also revealed by the N 1s XPS spectra (Figure 2c), where a shift of 0.3 eV was observed on CoPc-Gr as compared with the pristine CoPc [25]. However, Co 1s XPS of CoPc-Gr (Figure 2d) was the same as Gr, implying the insensitivity of the method due to the existence of vast amount of sp\textsuperscript{2} graphene carbon.

The obtained structural hybrids were used in the electrochemical detection of DA under the interference of high concentrations of AA. Steady-state cyclic voltammograms (CVs) (Figure 3a, inset) in the absence and presence of 1 mM DA showed that CoPc-Gr/GCE had an excellent response to DA. The CVs responses towards 1mM DA in 0.2 M phosphate buffer saline (PBS) were also measured for GCE, CoPc/GCE, GrO/GCE and Gr/GCE (Figure 3a). Well resolved, defined and more enhanced anode current peak could be observed on CoPc-Gr/GCE in reference to GCE, CoPc/GCE, GrO/GCE and Gr/GCE. Specifically, there was a 7 and 2 fold increase in current peak compared with those of unmodified electrode and Gr/GCE electrode, respectively. The potential difference (\Delta E\textsubscript{p}) between the anodic and cathodic peaks was 300 mV for the redox reaction of GCE, but \Delta E\textsubscript{p} of CoPc-Gr/GCE was one third of that of GCE, being the smallest amount among the tested CoPc-Gr/GCE, CoPc/GCE and Gr/GCE. This implies the fastest electron transfer rate of DA redox reaction on CoPc-Gr/GCE electrode [26]. In fact, the reduction process on CoPc-Gr/GCE was a two-step process as the oxidation product of DA, i.e. dopaminechrome was firstly transformed into leuco dopaminechrome and then further reduced to DA [27,28]. There was a relationship between pH value and the above mentioned phenomenon. Under relatively high or low pH value, the two reduction peaks merged into one peak, however, at proper pH value (pH = 4), the additional reduction peak appeared.
Figure 1. (a) UV-Vis spectra of Gr, CoPc-Gr and CoPc, (b) Raman spectra of CoPc-Gr, Gr, CoPc and graphite, (c) and (d) TEM images of Gr and CoPc-Gr, (e) SEM image of CoPc-Gr, (f) EDX profiles of surface (upper) and cross section (down) part of CoPc-Gr

Figure 2. XRD patterns of Gr and CoPc-Gr (a), XPS spectra of Co 2p (b), N 1s (c) and C 1s (d) region
CVs of DA are presented in Figure 3(c) on CoPc-Gr/GCE through the scan rate ranging from 5 to 100 mV/s. The relation between scan rates and the anodic currents predicted a single diffusion-controlled kinetic process even at high sweep rates to 100 mV/s as the current peak is proportional to the square root of the scan rate [29–31]. These phenomena suggest that CoPc-Gr can be applied as a sensitive sensor to determine the concentration of DA, because DA can easily diffuse through CoPc-Gr film. Square wave voltammogram (SWV) of DA and AA mixtures was carried out on CoPc-Gr electrode (Figure 3d). In the buffer solution containing 50 mM AA which is nearly 20000th times of the most diluted concentration of DA, peak current and the concentration of DA exhibited good linear relationship from 3 to 75 μM, showing the effectiveness of CoPc-Gr electrode in accurate determination of DA under the interference of AA.

Figure 3. (a) CVs on different types of electrodes in the presence of 1 mM DA (Inset: On CoPc-Gr/GCE in the absence (red line) and presence (green line) of 1 mM DA), (b) CVs on CoPc-Gr/GCE in the presence of 1 mM DA at different pH values, (c) CVs on CoPc-Gr/GCE in the presence of 1 mM DA at different sweep rates in 0.2 M PBS (pH = 4) at 50 mV/s (Inset: The line relation between peak currents and the square root of the scan rate), (d) SWV on CoPc-Gr/GCE in 0.2 M PBS (pH = 4) containing 50 mM VC and various concentrations of DA at 50 mV/s ([DA]: a = 3, b = 5, c = 25, d = 40, e = 50, f = 60, g = 75 μM; Inset: The relation between SWV currents and the concentrations of DA)

4. Conclusions

CoPc-Gr complex containing 14 wt% CoPc is synthesized and employed for electro-catalytic oxidation and accurate determination of DA in the interference of very high concentrations of AA. The modified CoPc-Gr electrode shows a better performance as compared with the reference electrodes such as Gr, CoPc or GrO, respectively. It can selectively determine the concentration of DA and possesses very low detection limit and broad linear range of response.

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References