ORIGINAL ARTICLE

Electrochemical behavior of brilliant cresyl violet at multi-wall carbon nanotubes/Nafion modified glassy carbon electrode and its interaction with cyclodextrins

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Abstract Multi-wall carbon nanotubes (CNTs)/Nafion composite membrane modified glassy carbon electrode (GCE) was fabricated to investigate the redox of brilliant cresyl violet (BCV) and its supramolecular system with γ-CD and hydroxypropyl-γ-CD (HP-γ-CD). The cyclic voltammetric results indicated that MWNTs/Nafion composite membrane was able to electrocatalyze the redox of BCV compared with bare GCE. Under optimal conditions, differential pulse voltammetry (DPV) was used to study the inclusion interaction of BCV with γ-CD and HP-γ-CD. The consequence demonstrated that the formation of complexes led to the rise of peak current and the shift of peak potential. The inclusion constants of BCV dimer with γ-CD, HP-γ-CD are 2,650 and 8,040 L/mol, respectively. UV–Vis spectra were also employed to confirm the formation of complexes. According to ^{1}HNMR, the possible binding mode of BCV dimer with CDs was discussed.

Keywords Brilliant cresyl violet · Carbon nanotubes · Modified electrode · Cyclodextrins · Supramolecular system

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Introduction

Carbon nanotubes (CNTs) have attracted intensive research due to their excellent electrical conductivity, mechanical strength, chemical stability, and flexibility [1]. These unique properties suggest that CNTs have the ability to promote electron transfer reactivity when used as an electrode material in electrochemical reactions [2]. So CNTs are widely used in electrochemistry as electrodes and as substrates for the fabrication of modified electrodes. For example, they have been utilized in the detection of DNA [3], estrogenic compounds [4], bilirubin oxidase [5], metal ion [6], medicine [7–9] with low detection limits and high sensitivity. However, since carbon nanotubes are large molecules with thousands of carbon atoms in an aromatic delocalized system, they are practically insoluble in all solvents, and as a result their applications are limited [10]. Up to now, the barriers of solubilizing CNTs have been greatly improved through their covalent or noncovalent functionalization [11]. In addition, wrapping CNTs by polymer chains is a new approach for achieving the solubility without any considerable impairment of their physical, chemical, and electrochemical properties [12]. Composite materials based on solubilizing CNTs with various polymers have been reported [13], one of which is Nafion. Because of the unique ion exchange, discriminative and biocompatible properties, Nafion films containing various electrocatalytic materials have been extensively applied in the modification of the electrode surfaces and in the construction of different functional biosensors. In present works, Nafion is used as a surfactant and as a binder to assist CNTs mechanical binding to the electrode [14].

Cyclodextrins (CDs) are cyclic oligosaccharides containing six, seven, and eight glucose units and are commonly called α-, β-, γ-cyclodextrins, respectively [15, 16].

Recently, natural and modified CDs have received much attention as aqueous-based hosts for studying the recognition of organic compounds [17], as they can alter the physical and chemical properties of guest molecules. In aqueous solution, equilibrium is established between uncomplex molecules and inclusion complexes. Frequently, guest and host combine to form two or more complexes which have different stoichiometries and stabilization. For example, CDs have become an important host molecule in dye industries because they can alter the solubility of dyes and shift equilibrium among dye monomer, dimer, and higher aggregate forms [18]. In addition, the formation of inclusion complexes of cyclodextrins with dyes can improve the rate of dyeing [19] and avoid effectively hydrolysis of colors in dye bath [20].

Herein, the electrochemical behavior of brilliant cresyl violet (BCV) on MWNTs/Nafion modified GCE was reported. The results revealed that the electrochemical signals of BCV on MWNTs/Nafion modified GCE can be enhanced due to the excellent properties of nanotubes. The electrochemical redox of BCV is a two-electron and two-proton process. We also found that the equilibrium between dye monomer and dimer was shifted with addition of γ-CD and HP-γ-CD, and the main state of BCV was a supramolecule of dimer with CDs. This phenomenon presents an agreement with the literature [21]. ^{1}HNMR spectrum further confirms the binding mode of BCV dimer with CDs, indicating that BCV dimer can form 1:1 inclusion complex with γ-CD and HP-γ-CD, respectively.

Experimental

Reagents

Multi-wall carbon nanotubes (MWNTs, average diameters ranged from 10 to 30 nm) were purchased from Shenzhen Bill Technology developing CO., LTD, and were purified according to the previous reference [22]. Nafion was obtained from Aldrich, and 0.1% ethanol solution was prepared. Brilliant cresyl violet (BCV) was purchased from Chroma-Gesellschaft Schmid & CO. γ-CD and hydroxypropyl-γ-CD (HP-γ-CD) was purchased from Aldrich. Stock solution of 1.0×10^{-2} mol/L CDs was prepared in double-distilled water. 6.8×10^{-2} mol/L Na$_2$HPO$_4$–KH$_2$PO$_4$ buffers of various pH values were used as the supporting electrolytes. All other reagents were analytical reagent grade and double-distilled water was used in all experiments.

Apparatus

A CHI 660C electrochemical workstation (Shanghai CH Instrument Company, China) was used for all of the electrochemical measurements such as cycle voltammetry (CV) and differential pulse voltammetry (DPV). A glassy carbon electrode (GCE) of 3-mm diameter was used as working electrode; a platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Ultraviolet–visible spectra were measured by employing TU-1901 spectrophotometer (Puxi instrument Company, Beijing, China). The measurement of ^{1}HNMR was performed on DKX-300 MHz (Bruker, Switzerland).

Procedures

Construction of the MWNTs/Nafion modified GCE

The surface of the working electrode was polished with 0.3 and 0.05 μm alumina/water slurries, washed with double-distilled water, and finally ultrasonicated for 5 min before use. 1 mg purified MWNTs were dispersed in 10 mL 0.1% Nafion ethanol solution with the aid of ultrasonication to form 0.1 mg/mL MWNTs/Nafion black solution. Then, the MWNTs/Nafion modified GCE was fabricated by casting 5.0 μL of the suspension on the surface of the treated GCE and dried at the room temperature. The modified GCE was transferred to the electrolytic cell for further activating by using cyclic voltammetry between −0.8 and 0.2 V at a scan rate of 0.1 V/s in Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer (pH 6.2) until a stable cyclic voltammetric profile was obtained.

Voltammetry measurement

Cyclic voltammograms of BCV were recorded at a scan rate of 0.1 V/s on unmodified and modified GCE. Measurements were carried out in Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer (pH 6.2). The scan potential ranged from −0.8 to 0.2 V. All measurements were performed at room temperature. Differential pulse voltammetry was used to determine the inclusion complex of BCV with CDs under optimal condition. After the electrochemical experiments for BCV were completed, appropriate amount of CDs were added to the system and electrochemical signals were recorded after reaction for 10 min.

Ultraviolet–visible spectra measurement

Ultraviolet–visible spectra were measured by employing TU-1901 spectrophotometer at room temperature. Then, appropriate amount of CDs were added to the quartz cell. Ultraviolet–visible spectra were recorded by using the same parameters as in the first scan after reaction for 10 min.

Results and discussion

Electrochemical behavior of BCV

In this paper, a nanostructured modified glassy carbon electrode was investigated. Markedly different electrochemical behavior of BCV was observed depending on whether the glassy carbon electrodes used were unmodified, modified with Nafion film, or modified with MWNTs/Nafion film. Figure 1 showed the cyclic voltammograms of different kinds of modified GCEs in Na_2HPO_4–KH_2PO_4 buffer (pH 6.2). Two pairs of quasi-reversible cyclic voltammetric peaks (curve a) were found on bare GCE at $Ep_{a1} = -193$ mV and $Ep_{a2} = -377$ mV (corresponding to cathodic peaks $Ep_{c1} = -234$ mV and $Ep_{c2} = -416$ mV, respectively) at the scan rate of 0.1 V/s. The peak-to-peak potential differences (ΔEp) were 41 mV and 39 mV, respectively. The above peaks correspond to the reaction of the N atom at position 1 and position 2 (Fig. 2). Curve b show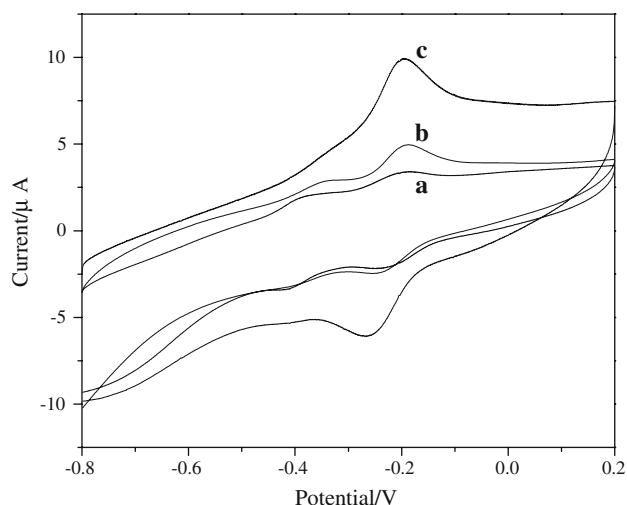ed the cyclic voltammo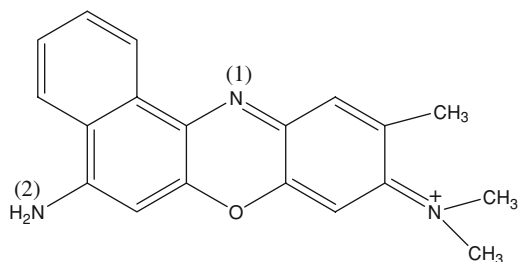gram of BCV on Nafion film modified GCE. The results demonstrated a positive shift of two anodic peaks and a negative shift of two cathodic peaks. However, in this case the increase of the peak current at -193 mV was observed. It can be ascribed as follow: Nafion is a kind of polyanionic polymer. It possesses a polar side chain which act as an ion exchange [23], as a result, the positive charge of BCV molecular are easily exchanged on the surface of Nafion modified GCE, and the peak current at -193 mV can greatly be enhanced. For MWNTs/Nafion modified GCE, the voltammogram (curve c) indicated a well-defined quasi-reversible redox peak only at $Ep_a = -194$ mV and $Ep_c = -267$ mV as well as the negative shifts of anodic and cathodic peak potentials. It was also interesting to note that the background current increased at modified GCE. The peak at -377 mV was hardly observed. The possible explanation could be the fact that the functional carbon nanotubes possess –COOH and –OH groups, they can form hydrogen bond with H atom at position 2 of BCV molecule. On the other hand, the excellent electrocatalysis ability of CNTs promotes electron transfer reactivity to result in the increase of peak current.

Figure 3 showed the cyclic voltammograms of BCV in Na_2HPO_4–KH_2PO_4 buffer (pH 6.2) at the different scan rates. A pair of roughly symmetric anodic and cathodic peaks appeared with almost equal peak currents in the range from 0.04 V/s to 0.3 V/s. With the increase of the scan rate the peak-to-peak potential differences also increased. By measuring the dependence of the cathodic peak potentials (on MWNTs/Nafion modified GCE) versus the log of the scan rate, the electron numbers can be estimated by the following equation [24]:
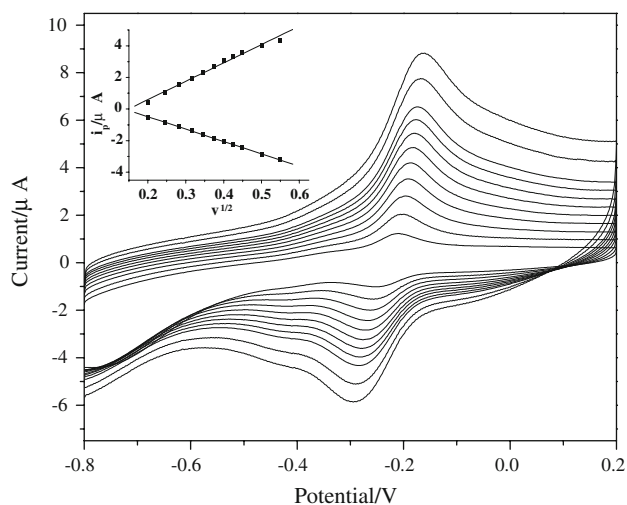

Fig. 1 Cyclic voltammograms of 2.0×10^{-5} mol/L BCV in pH 6.2 Na_2HPO_4–KH_2PO_4 buffer **a** bare GCE, **b** Nafion film modified GCE, **c** MWNTs/Nafion modified GCE

Fig. 2 The structure of BCV

Fig. 3 Cyclic voltammograms of 2.0×10^{-5} mol/L BCV in pH 6.2 Na_2HPO_4–KH_2PO_4 buffer. Scan rate (from inner to outer) 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, and 300 mV/s. Insert: The relation between the peak currents with scan rates

$$E_{pc} = B - \frac{RT}{\alpha nF} \ln v$$

Where R is the gas constant, α is the transfer coefficient, n is the number of electrons, F is the Faraday constant, and B is a constant. We calculated that α is 0.61 and n is 2. The i_p versus $v^{1/2}$ plot shown in the insert of Fig. 3 exhibited a linear relationship indicating that the redox process was a quasi-reversible diffusion controlled process.

The pH effects on the electrochemistry of BCV were examined. Figure 4 presented the effect of pH values on the peak currents of BCV. It was found that the anodic peak currents of BCV increased gradually with pH values increasing from 5.0 to 6.2, and maintained constant from 6.2 to 7.0, however, when pH values are higher than 7.0, the peak currents decreased rapidly. It implied that BCV was apt to redox in weak acid medium. Therefore, pH 6.2 was selected for further experiment. In addition, the ratio of the electron numbers to the proton numbers during the redox reaction was determined. It can be seen that a linear relationship was found in the pH range from 5.0 to 9.2 with a slope of 59.6 mV/pH. The slope was close to the theoretical value of 59 mV/pH, which indicated that the numbers of protons and electrons involving in the electrode process are equal. So, the electrochemical redox of BCV can be simply expressed as follows (Fig. 5).
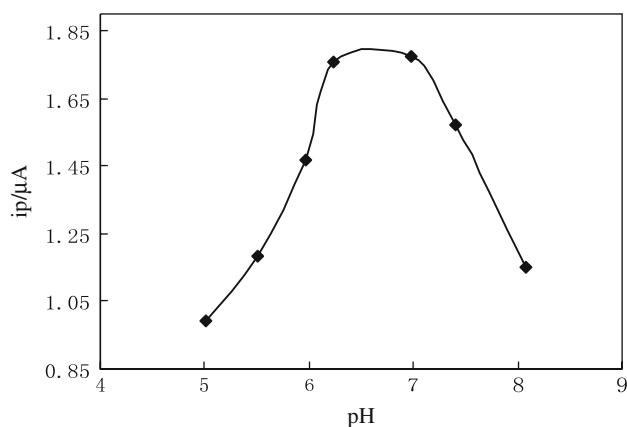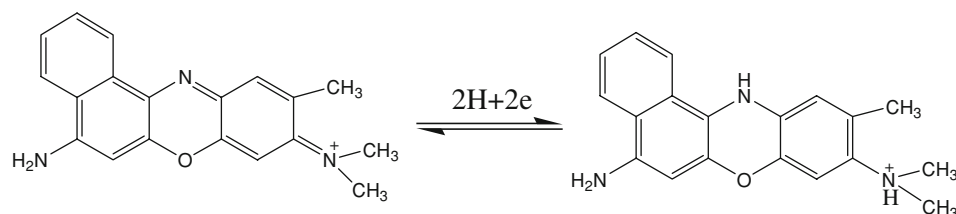
Host–guest complexation of BCV with cyclodextrins

The effect of CDs on the electrochemical properties of various electroactive species included in the cavity has been reported [25]. In the experimental measurements, differential pulse voltammetry was employed to determine the formation constants between host and guest. The differential pulse voltammogram (DPV) in Fig. 6 showed that anodic peak potential of BCV is at −258 mV. With addition of γ-CD, the anodic peak potential shifted 2 mV toward positive potential and the peak current increased markedly. The results suggest that the supramolecular system were formed between BCV and γ-CD. Inclusion by γ-CD promoted BCV aggregation toward dimer in aqueous solution, the electrochemical response mainly came from the redox of the H-aggregation which possess more reaction site, as a result, it inevitably lead to an increase of the peak currents.

Literature [21] have revealed that the cationic dyes tend to aggregate in the concentration range used ($10^{-3} \sim 10^{-6}$ mol/L), and mainly exist monomer–dimer equilibrium. If the aggregation state equilibrium tends to the formation of dimer and even higher-order aggregates, the absorption peak will shift to the blue wavelength. From Fig. 7 it can be seen that the dyes mainly exist as monomer
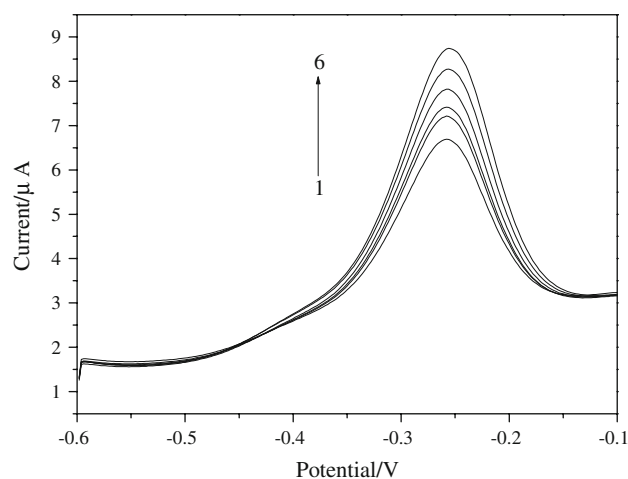
Fig. 6 Differential pulse voltammograms of 1.0×10^{-5} mol/L BCV in pH 6.2 Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer contain different concentrations of γ-CD. Concentration of γ-CD: (1) 0; (2) 2.0×10^{-5}; (3) 4.0×10^{-5}; (4) 8.0×10^{-5}; (5) 1.2×10^{-4}; (6) 1.6×10^{-5} mol/L

Fig. 4 The effect of pH on peak current

Fig. 5 The redox mechanism of BCV
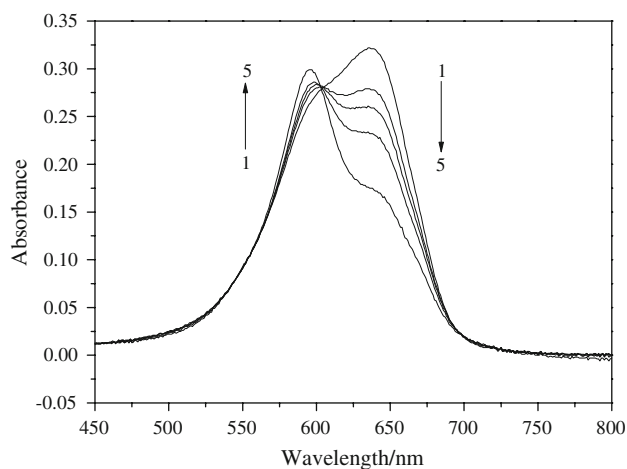
Fig. 7 Absorption spectra of 1.0×10^{-5} mol/L BCV in pH 6.2 Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer contain different concentrations of γ-CD. Concentration of γ-CD: (1) 0; (2) 1.7×10^{-5}; (3) 3.3×10^{-5}; (4) 6.7×10^{-5}; (5) 4×10^{-4} mol/L

Fig. 9 The possible geometry of the BCV dimer with γ-CD

at 636 nm, with addition of γ-CD, dimer will gradually increase in solution, the peak at 636 nm continuous declined and the peak at 599 nm gradually increased. Thus, the peak at 599 nm was the characteristic value of BCV dimer. The results implied that the main state of BCV is monomer in solution without γ-CD. However, the main state of BCV is supramolecule of BCV dimer with γ-CD in the presence of γ-CD because two BCV molecules form H-aggregation in the cavity of γ-CD.

The increase of peak current confirm that the complexes of BCV dimer with γ-CD is electrochemically active, if it is assumed that the variation value of the peak current is proportional to the concentration of complexes. The formation constants β were determined by using the following equation [26–29]:

$$\frac{1}{\Delta i_p} = \frac{1}{\Delta i_{max}} + \frac{1}{\Delta i_{max} \beta [CD]^m}$$

Where Δi_p stands for the variation of peak current after forming inclusion complexes, Δi_{max} is the peak
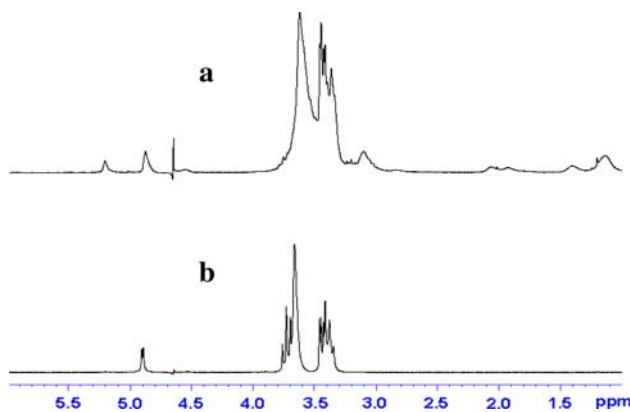
current in case of complete BCV complexing, [CD] is the concentration of the CD, β is the inclusion constant and m is the inclusion ratio. If BCV dimer and CDs only form a complex dimer-CD$_m$, the plots of $1/\Delta i_p$ versus $1/[CD]^m$ should give some curves when m is 1, 2, 3…, respectively. From above formula, the results showed that the binding ratio of BCV dimer with γ-CD and HP-γ-CD are both 1:1, and inclusion constants are 2,650 and 8,040 L/mol, respectively. The experimental data demonstrated that modified γ-CD afford the strong binding ability with guest molecule than native γ-CD. Strong inclusive ability can be understood that the substitution by hydroxypropyl destroy the strong hydrogen bond network, which make it easier for guest molecules to gain access to modified CDs cavity and to have bigger inclusion constants.

Discussion of binding mode

To estimate the possible complex mode of γ-CD with guest molecule, ^{1}HNMR was performed to investigate the structure of the host–guest inclusion complex by changes of the chemical shifts of the relevant protons in ^{1}HNMR spectra. The ^{1}HNMR of γ-CD and the complexes of BCV dimer with γ-CD were shown in Fig. 8. The results displayed obvious chemical shifts of the H-3 (0.522 ppm) and H-5 (0.261 ppm) protons of γ-CD. Since both the H-3 and H-5 protons are located at the interior of γ-CD cavity and H-5 protons are located near the narrow side of cavity, but the H-3 protons near the wide side of cavity, indicating that BCV dimer may enter the cavity of γ-CD from the wide side. According to the ^{1}HNMR and the structure of BCV dimer, the possible spatial configuration about the inclusion complex of BCV dimer with γ-CD was shown in Fig. 9.

Conclusions

In this paper, MWNTs/Nafion film coated GCE was fabricated for the study of the electrochemical behavior of brilliant cresyl violet and its interaction with γ-CD and HP-γ-CD. Owing to the high specific surface area, subtle

Fig. 8 ^{1}HNMR spectra (300 MHz, D$_2$O) of **a** BCV-γ-CD and **b** γ-CD

electronic properties and strong adsorptive ability of MWNTs, the modified GCE can greatly enhance the redox peak current of BCV. The BCV dimer can form 1:1 inclusion complexes with γ-CD and HP-γ-CD. The inclusion constants are 2,650 and 8,040 L/mol, respectively. The results indicated that the major factor affecting inclusion ability is size matching between CDs and guest. Furthermore, the sensitive and simple chemically modified electrode was proved to be available and easy to fabricate for researching the electrochemical behavior of cation dyes and the supramolecular system.

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