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Improved Voltammetric Response of Malachite Green at a Multi-Walled Carbon Nanotubes Coated Glassy Carbon Electrode in the Presence of Surfactant

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Malachite green (MG) can exhibit an anodic peak at multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrodes (GC). When surfactant cetylpyridinium bromide (CPB) is introduced in the MG solution, the electrode is modified by CPB further due to its adsorption, and the anodic peak current of MG increases greatly. Meanwhile, the peak potential moves from 0.42 V to 0.62 V (vs. SCE). Parameters influencing the voltammetric response of MG are optimized. Under the selected conditions (i.e. preconcentration for 180 s at -0.5 V, in 0.10 M pH 7.0 phosphate buffer containing 4×10^{-5} M CPB), the anodic peak current is proportional to MG concentration in the range of 1×10^{-9} - 5×10^{-6} M, with a detection limit of 9×10^{-10} M. This method possesses good reproducibility and stability, and it is applied to the determination of MG in pond water. In addition, the voltammetric response of MG at a GC modified with MWCNTs and insoluble cationic gemini surfactant (i.e., $C_{12}H_{25}N(CH_3)_2–C_{12}H_{24}–N(CH_3)_2C_{12}H_{25}Br_2$, $C_{12}–C_{12}–C_{12}$) is tested in solutions without CPB, similar results are obtained. Therefore, it is an alternative way to fabricate sensitive sensor by combining carbon nanotubes with surfactants.

Keywords: Cetylpyridinium bromide, malachite green, multi-walled carbon nanotubes, voltammetry, gemini surfactant

1. INTRODUCTION

Malachite green (MG) is a synthetic triphenylmethane dye [1]. It was generally used to control external fungal and protozoan infection of fish. However, MG has potential carcinogenicity, mutagenicity and teratogenicity in mammals [2], hence it can cause negative side effect on man who eats the fish since MG and its reduced product - leucomalachite green (LMG) could remain in fish tissue for extended period of time. Although MG has not been granted as a veterinary drug for use, it is still applied illegally sometimes due to its low cost, easily availability and high efficacy [3]. Therefore, the detection of MG is important. High performance liquid chromatography (HPLC) is currently used for MG determination [4-6]. Considering the high sensitivity, rapid detection and low cost of electrochemical method, researchers tried to apply it in MG determination. For example, Yi et al determined MG with a multi-walled carbon nanotubes modified glassy carbon electrode; the detection limit was 6.0×10^{-9} M after 5 min accumulation [7]. Ngamukot et al developed a boron-doped diamond thin-film electrode for the determination of MG [8], the linear range was 1×10^{-6} - 1×10^{-4} M and the detection limit was 5×10^{-8} M. However, to the best of our knowledge, the surfactant/MWCNTs film modified electrode has not been used for this purpose**.**

Surfactants are widely applied in electrochemistry to improve the property of the electrode/solution interface [9-11]. It was reported that in the presence of some surfactants the detection sensitivity of many analytes was enhanced [12-15]. In this work, a simple surfactant/MWCNTs film modified electrode is attempted for MG assay. The electrode presents good analytical performance and application potential.

2. EXPERIMENTAL PART

2.1. Reagents

The multi-walled carbon nanotubes used (diameter <10 nm, length 1-2 µm, purity ≥95%) came from Shenzhen Nanotech. Port Co. Ltd. (Shenzhen, China). Malachite green, tetradecane- pyridinium bromide (TPB), tetradecanepyridinium chloride (TPC), cetylpyridinium bromide (CPB), Triton X-100, cetyltrimethyl ammonium bromide (CTAB), octadecyltrimethyl ammonium bromide (OTAB) and sodium dodecyl sulfate (SDS) were obtained from Chemical Factory of Shanghai (China). Gemini surfactants butyl-α,ω-bis (dimethyldodecylammonium bromide) ($C_{12}H_{25}N(CH_3)_2$-$C_{12}H_{24}$-$N(CH_3)_2C_{12}H_{25}Br_2$, C_{12}-C_{12}-C_{12}) was synthesized and purified according to literature [16]. Other chemicals used were of analytical grade. The water used was redistilled.

2.2. Apparatus

The voltammetric experiments were performed with a CHI 830 electrochemical workstation (CH Instrument Company, Shanghai, China). A conventional three-electrode system was used. The working electrode was a modified glassy carbon electrode (GCE, 3 mm in diameter); a platinum wire and a saturated calomel electrode (SCE) were employed as auxiliary electrode and reference electrode, respectively.

2.3. Preparation of modified GCE

Pure MWCNTs was pretreated according to the literature [17]. Then 10 mg pretreated MWCNTs was dispersed in 10 mL water with the aid of ultrasonication agitation to proper homogeneous suspension. Before modification, the GCE was polished with aluminum oxide slurry on chamois leather, rinsed thoroughly with water, and ultrasonicated in water for 2 min. Then 3 μL of the MWCNTs suspension was transferred to the GCE surface and dried under an infrared lamp. Thus, a uniform film coated GCE was obtained. For comparison, 2 μL C_{12}-C_{12}-C_{12} solution was added on the MWCNTs/GCE to fabricate C_{12}-C_{12}-C_{12}/MWCNTs/GC electrode.

2.4. Experimental procedure

Appropriate volume of MG (or MG and CPB) stock solution was transferred into a cell containing 10 mL of 0.10 M phosphate buffer solution (pH=7.0), and then the three-electrode system was installed on it. After preconcentration at -0.5 V for 180 s under stirring, the voltammograms were recorded between 0.2 and 1.0 V at scan rate of 0.10 Vs^{-1}. Following this, the solution was replaced by a blank solution and the potential scan was repeated for several times for the electrode to regenerate.

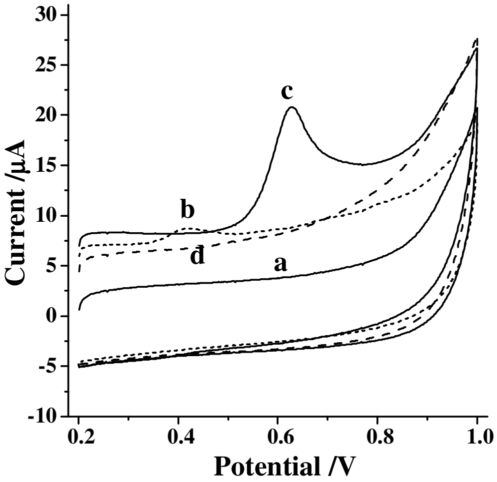

Figure 1. Cyclic voltammograms of MWCNTs/GCE in solution containing: (a) 0.1 M pH 7.0 phosphate buffer solution, (b) a plus MG, (c) a plus CPB and MG, (d) a plus CPB. Scan rate: 100 mVs^{-1}; accumulation time: 180 s; accumulation potential: -0.5 V; MG concentration: 2×10^{-6} M; CPB concentration: 4×10^{-5} M.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammogram of MG

Figure 1 shows the cyclic voltammograms of MG at MWCNTs/GCE. As can be seen MG exhibits a small anodic peak at 0.42 V in pH 7.0 phosphate buffer solution (curve b). After adding 4×10^{-5} M CPB, the peak at 0.42 V disappears, and a bigger anodic peak occurs at 0.62 V. However, CPB does not produce any peaks in the potential range. Thus the anodic peak at 0.62 V should be ascribed to the oxidation of MG. It means that CPB makes the oxidation of MG more difficult while it allows more MG to take part in electrochemical reaction. This is thought to result from the adsorption of CPB on the electrode surface and its promotion effect on the accumulation of MG. Thus the MWCNTs/GCE virtually becomes CPB/MWCNTs/GCE due to the on-line modifying of CPB. This point is partly supported by the absorption spectrum experiment. The absorption peaks of MG keep almost unchanged when CPB is present, implying that the enhanced accumulation is not due to the formation of complex. As to the change of peak potential, it can be attributed to the hindrance of adsorbed CPB to electron transfer of MG.

3.2. Comparison of various surfactants

The influence of various surfactants is investigated (Fig. 2). In the presence of Triton X-100 and SDS, the anodic peak of MG decreases and the peak shape becomes bad-defined. However, when cationic surfactant is present, the peak increases greatly and the peak potential shifts positively. As MG holds positive charges, the effect of cationic surfactant on MG accumulation should not be ascribed to electrostatic attraction but hydrophobic interaction or others. Among the surfactants used CPB makes the peak current increase most, which may be related to the strong surface activity of CPB.

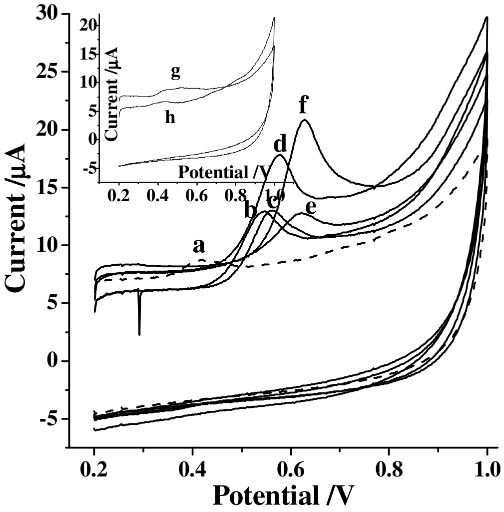

Figure 2. Influence of surfactant on the voltammogram of MG. Solution condition: 0.10 M PBS + 2×10^{-6} M MG + 0, 4×10^{-5} M TPB, TNC, CTAB, OTAB, CPB, Triton-X-100 or SDS (from a to h). Other conditions are as Fig.1.

3.3. Influence of CPB concentration

Figure 3 displays the influence of CPB concentration. The peak current of MG increases with CPB concentration rising and reaches a maximum around 4×10^{-5} M. Further increasing CPB concentration makes the peak current decrease. Meanwhile, the peak moves in positive direction. This is related to the change of adsorbed amount of CPB. When its concentration is smaller the adsorbed amount of CPB is smaller, the amount of MG accumulated increases with CPB concentration growing.

When CPB concentration is high enough the amount of MG accumulated no long increases, while the more dense CPB adsorbed layer shows increasing hindrance to the electron transfer of MG adsorbed. Accordingly, the peak current decreases and the peak potential become more positive.

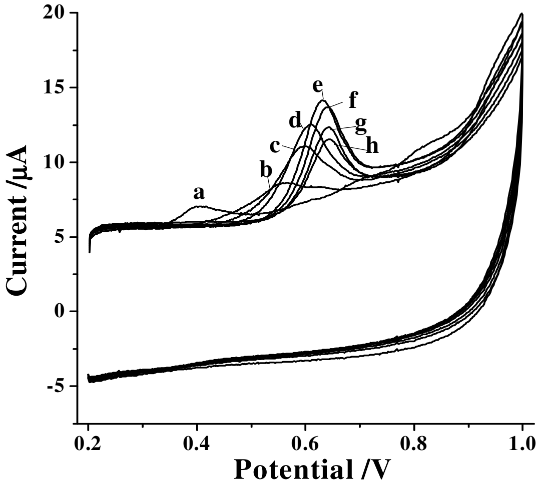

Figure 3. Variation of peak current and peak potential with CPB concentration. Concentration of CPB (from a to h): 0, 1× 10^{-5} , 2× 10^{-5}, 3× 10^{-5} , 4× 10^{-5} , 5× 10^{-5} , 6× 10^{-5} , 7× 10^{-5} M. Other conditions are as Fig.1.

3.4. Influence of pH

The effect of pH on the peak current and peak potential is studied by cyclic voltammetry. As shown in Fig. 4, the peak potential is almost independent of pH in the range from 5 to 10. It seems that no proton is involved in the electrochemical reaction. This may relate to the slow proton transfer since the redox reaction of MG logically involves proton transfer. The peak current varies with pH and it reaches a maximum around pH 7. It means that pH influences the accumulated amount of MG.

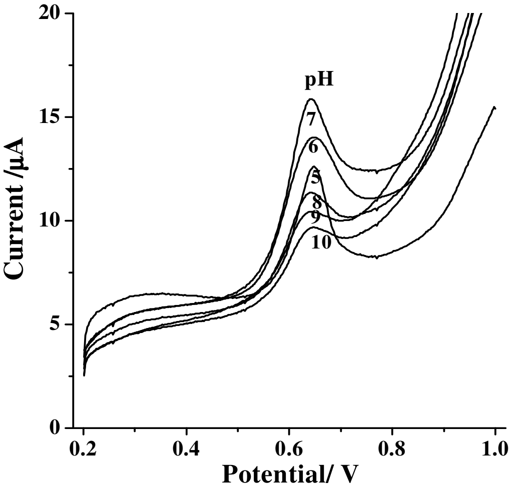

Figure 4. Cyclic voltammograms of MWCNTs/GCE in solution containing 2×10^{-6} M MG, 0.10 M PBS and 4×10^{-5} M CPB. Solution pH: 5, 6, 7, 8, 9, 10. Other conditions are as Fig.1.

3.5. Influence of accumulation time and accumulation potential

As shown in Fig. 5, when the accumulation potential shifts from -0.8 to 0.5 V, the peak current of MG varies markedly. At -0.5 V the peak current of MG achieves a maximum. This can be attributed to the electrostatic interaction between electrode and MG. At pH 7.0 MG holds positive charges, thus proper negative potential benefits its accumulation at electrode surface. As can be seen in Fig. 5B, the peak current of MG increases with prolonging accumulation time and it reaches a maximum at 180 s for 2×10^{-6} M MG. Beyond 180 s, the peak current keeps almost unchanged, indicating that a saturated accumulation is achieved at the electrode surface.

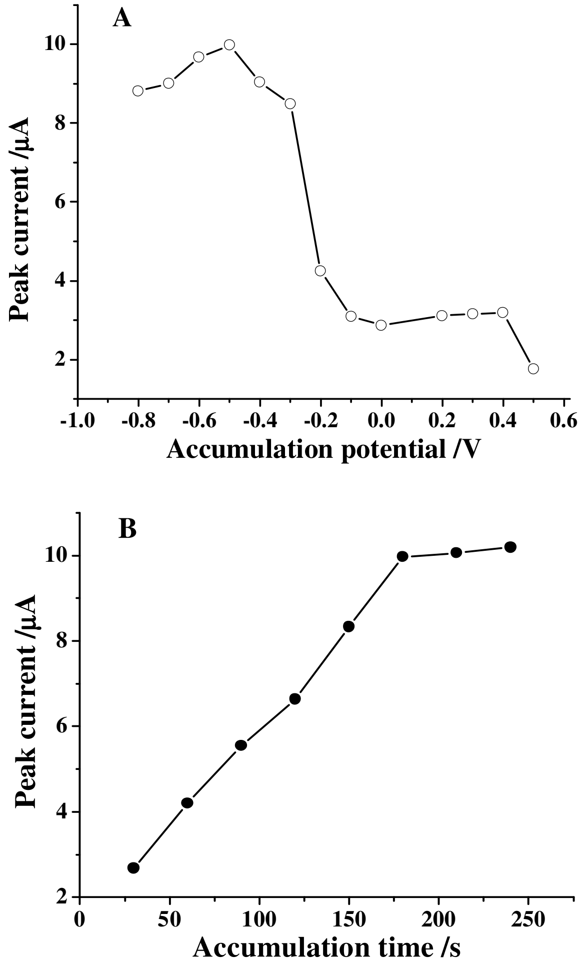

Figure 5. Effect of accumulation potential (A) and accumulation time (B) on the peak current. Other conditions are as Fig.1.

3.6. Influence of scan rate

The anodic peak current of MG changes linearly with scan rate (Fig. 6), the regression equation is $i_{pa} = 1.01 + 51.5v$ (i_{pa} in μA, v in Vs^{-1}, r = 0.998). This indicates that an adsorption- controlled electrode process occurs at the modified electrode. With increase of v, the peak potential (E_{pa}) shifts positively and there is a linear relationship between them, the regression equation is: $E_{pa} = 0.714 + 0.0703 \log v$ (E_{pa} in V, v in Vs^{-1}, r = 0.996). According to the following equation [18]:

$$E_{pa} = E_0 + (\frac{2.303RT}{\alpha nF})\log(\frac{RTk^0}{\alpha nF}) + (\frac{2.303RT}{\alpha nF})\log \upsilon$$

The αn is calculated to be 0.84. Suppose that α equal to 0.5 for a totally irreversible electrode process, n is ca. 2.

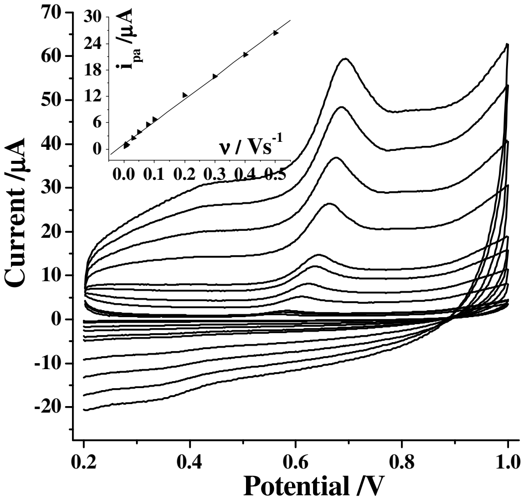

Figure 6. Cyclic voltammogram of MWCNTs/GCE at different scan rate. Scan rate (from inner to outer): 0.005, 0.008, 0.01, 0.02, 0.05, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5 Vs^{-1}. Other conditions are as Fig.1

3.7. Chronocoulometrc response

The chronocoulometric response of MG is recorded. After subtraction of the background charge, the Q and the square root of time ($t^{1/2}$) present linear relationship. According to the integrated Cottrell equation [19]:

$$Q = 2nFAcD^{1/2}\pi^{-1/2}t^{1/2}$$

The apparent diffusion coefficient (D) of MG can be calculated from the slope of Q versus $t^{1/2}$ plot. In this case, $A = 0.0676$ cm^2, n = 2 and $c = 2\times10^{-6}$ M, the values of slopes are 4.89 $\mu Cs^{-1/2}$ (in the presence of CPB) and 1.22 $\mu Cs^{-1/2}$ (in the absence of CPB), respectively. Hence D equals 1.71×10^{-7} cm^2 s^{-1} (without CPB) or 2.74×10^{-6} cm^2 s^{-1} (with CPB). This may result from the influence of CPB on the active electrode area and the solution property. According to the equation $Q_{ads} = nFA\Gamma$, the surface coverage Γ of MG on the modified electrode can be evaluated based on the intercept of the plot of Q versus $t^{1/2}$. Without CPB, the value of Γ is 9.25×10^{-11} mol cm^{-2}. After addition of CPB, Γ increases to 7.67×10^{-10} mol cm^{-2}. Therefore, the voltammetric response of MG is enhanced markedly.

3.8. Calibration curve

Figure 7 shows the dependence of the anodic peak current on MG concentration. They show good linear relationship in the range of 1 × 10^{-9} to 5 × 10^{-6} M. The regression equations are: i_{pa} = 0.436 +33.5 c (i_{pa} in μA, c in μM, r=0.998, for the range of 0.001-0.01μM ,) and i_{pa} = 1.19 +3.59 c (r=0.998, for the range of 0.01-5 μM). The detection limit is estimated to be 9 × 10^{-10} M (S/N = 3) after 180 s accumulation at -0.5 V. This modified electrode shows good reproducibility. A relative standard deviation (RSD) of 2.38% is obtained for the detection of a 2× 10^{-7} M MG (n=10). When the solution is measured with five electrodes individually fabricated the RSD of peak current is 2.93%.

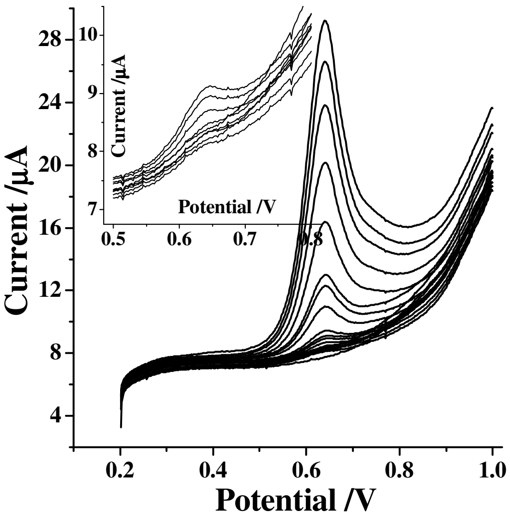

Figure 7. Cyclic voltammogram of MWCNTs/GCE in solution containing different concentration of MG. MG concentration: 0, 0.001, 0.002, 0.005, 0.007, 0.01, 0.02, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 μM (from inner to outer); inset: the zoomed overlay lines (concentration: 0.001, 0.002, 0.005, 0.007, 0.01, 0.02, 0.05, 0.08, 0.1μM). Other conditions as in Fig. 1.

3.9. Determination of sample

Pond water sample was determined. Prior to determination the water sample was filtered with filter paper to remove alga. Then 2 mL water sample was transferred to a cell containing 8 mL 0.10 M PBS and 40 μL 0.010 M CPB for voltammetric determination. A standard addition method was adopted to assess the reliability. The results are summarized in Table 1. The recoveries of the MG standards added are 97.5% to 99.3%.

3.10. Voltammetric response of MG at C_{12}-C_{12}-C_{12}/MWCNTs/GC

Considering the influence of CPB in solution on the response of MG, a modified electrode containing MWCNTs and insoluble cationic surfactant (i.e. C_{12}-C_{12}-C_{12}) is tested. As a result, the modified electrode also displays enhanced response to MG, although CPB is absent. But the response is not as sensitive as that mentioned above. This is related to the surfactant used, and to prepare a sensitive electrode a proper insoluble surfactant should be adopted.

Table 1. Determination result of MG in pond water [a]

Added (M)	Expected (M)	Found (M)	Recovery (%)	Ref. value (M)[b]
0.0	-	ND	-	ND
1.0×10^{-7}	1.0×10^{-7}	9.87×10^{-7}	98.7	
2.0×10^{-7}	2.0×10^{-7}	1.95×10^{-7}	97.5	
3.0×10^{-7}	3.0×10^{-7}	2.98×10^{-7}	99.3	

[a] Number of sample assayed: 3.

[b] Measured with UV-Vis absorption spectroscopy at 623 nm.

4. CONCLUSIONS

Malachite green (MG) can exhibit an anodic peak at MWCNTs modified glassy carbon electrodes. When surfactant cetylpyridinium bromide (CPB) is introduced in the solution, the electrode is modified by CPB further due to its adsorption, the anodic peak current of MG increases greatly. Meanwhile, the peak potential shifts positively. Based on this, a simple and sensitive electrochemical method can be developed for the determination of MG. This modified electrode has good reproducibility and stability. When a insoluble cationic surfactant (e.g. geminis C_{12}-C_{12}-C_{12}) is introduced in the coating film, the resulting surfactant/MWCNTs/GC electrode also shows enhanced response to MG, although CPB is absent in the solution. Therefore, the surfactant/MWCNTs/GC is promising.

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