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# Poly(malachite green) film: Electrosynthesis, characterization, and sensor application

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## Abstract

Poly(malachite green) films were synthesized electrochemically on the glassy carbon electrode in the potentiodynamic mode. The characterization and growth mechanism of as-prepared films were studied with FT-IR spectroscopy, UV–vis spectroscopy, cyclic voltammetry, chronocoulometry, and electrochemical impedance spectroscopy. Charge transfer and ion transport of poly(malachite green) films were investigated in the aqueous solutions with different types of supporting electrolytes. The poly(malachite green) film coated glassy carbon electrode showed catalytic ability towards ascorbic acid and dopamine. The difference of the anodic peak potential of ascorbic acid on the poly(malachite green) film modified electrode from that of dopamine was 180 mV. Based on their voltammetric responses, the poly(malachite green) film coated glassy carbon electrode was utilized as an electrochemical sensor for the content determination of ascorbic acid and dopamine simultaneously and separately in pharmaceutical and injections.

*Keywords:* Conducting polymer; Electrosynthesis; Malachite green

## 1. Introduction

Synthesis [1–9], characterization [1,9–11], properties' investigation [1,6,7,9–14], and application exploiture [16–23] of electronically conducting polymers (e.g. polyconjugated, polyaromatic, and polyheterocyclic macromolecules) continue to be a hot topic for physicists and chemists, especially for electrochemists. Physicists pay more attention to the properties (mainly the conductivity) of doped/undoped conducting polymers in their dry state [9,22,23] whereas the electrochemists are interested in their fundamental features (e.g. ion transport [9,15], charge transfer [9,15], catalysis [9,10,16]) when polymer films are in contact with electrolyte solutions by coating these electronically conducting polymers onto various substrate electrodes.

Electronically conducting polymer film coated electrodes have shown their amazing but complicated features and various applications [9,10]. The electronically conducting polymers used for these investigations are always generated electrochemically [9,16] in the potentiostatic (applying constant potentials on electrodes), potentiodynamic (scanning potential of electrodes), and/or galvanostatic mode (altering the current density of electrodes). The as-prepared polymer film coated electrodes have been characterized by various techniques [9,10,16], e.g. FT-IR spectroscopy, UV–vis spectroscopy, atomic force microscopy (AFM), X-ray diffraction (XRD), electrochemical quartz crystal microbalance (EQCM), electrochemical impedance spectroscopy (EIS), and scanning electrochemical microscopy (SECM) [24–27]. The fundamental

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topics on polymer film coated electrodes have covered the nature of charge transfer and/or ion transport at polymer–electrolyte interfaces and/or through the polymer layer during their oxidation and reduction [9,15], the theoretical treatment of parameters determining the rates of both charge transfer [9,15], and the possible catalytic properties and catalytic process towards species in the solution [9,10,16,20,28,29]. Various kinds of practical applications of polymer film coated electrodes have also been reported including the use in the field of catalysis [10], electronic devices [13,23], electrochromic displays [1,23], light emitting setups [22], chemical and biochemical sensors [10,20,21], and energy conversion and storage [19,23]. Especially the utilization of polymer film coated electrodes as chemical and biochemical sensors has been studied extensively and successfully [10,20,21]. Taking the design of sensor for small organic bio-molecules (e.g. ascorbic acid and dopamine) as an example, Zare and coworkers electrochemically polymerized oracet blue on the glassy carbon electrodes and the resulting polymer film coated electrode shows catalytic ability towards dopamine, ascorbic acid, and uric acid [28]. Zhang et al. determined dopamine in the presence of ascorbic acid using the glassy carbon electrode modified with poly(styrene sulfonic acid) film and single-wall carbon nanotube [29]. Poly(hippuric acid) [30], poly(2-picolinic acid) [31], poly(*p*-aminobenzenesulfonic acid) [32], poly(amidosulfonic acid) [33], and poly(*o*-aminobenzoic acid) [34] film-coated electrodes have also been developed by Zhang et al. to monitor dopamine in the presence of ascorbic acid.

The polymer of interest here is poly(malachite green) which is possibly a novel polymer since until now there are no reports relating to its synthesis, characterization, and properties' investigation, to our best knowledge. Poly(malachite green) may be generated by electrochemical polymerization of malachite green, the chemical structure of which is illustrated in Fig. 1. Malachite green has an open but ionized structure, and hence the resulting polymer is promising in exhibiting interesting features like fast rate of charge transfer and ion transport and nice catalytic ability towards small bio-molecules. Therefore in this contribution we reported the polymerization of malachite green potentiodynamically on the glassy carbon electrode, investigated the possible growth mechanism of poly(malachite green) film, and studied the electrochemical properties (e.g. charge transfer, ion transport, catalytic ability towards ascorbic acid and dopamine) of poly(malachite green) film on the glassy carbon electrode by use of optical (FT-IR spectroscopy and UV–vis spectroscopy) and electrochemical techniques (cyclic voltammetry, chronocoulometry, and electrochemical impedance spectroscopy).

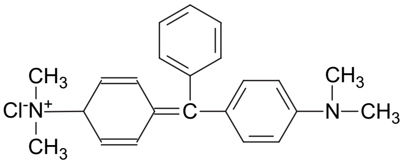

Fig. 1. Chemical structure of malachite green.

## 2. Experimental

### 2.1. Chemicals and solutions

Malachite green (Tianjin Chemical Co., Tianjin, China), ascorbic acid (Shanghai Chemical Co., Shanghai, China), and dopamine (Acros Organic Co., USA) are analytical grade reagents and are used as received without further purification. Other chemicals like sulfuric acid, nitric acid, chloride acid, $NaNO_3$, NaOH, $K_2HPO_4$, $KH_2PO_4$, $KNO_3$, $KClO_4$, LiCl, NaCl, KCl, and $NH_4Cl$ purchased from Shanghai Chemical Co., Shanghai, China are of analytical grade and are used as received without special treatment.

All the solutions were prepared with double-distilled water and the solutions for electropolymerization of malachite green and voltammetric experiments were deoxygenated with highly purified nitrogen at least for 20 min and always kept under nitrogen atmosphere. Several buffer solutions were prepared and adjusted by a pH meter before measurements. The solutions used for recording the UV–vis spectra of poly(malachite green) and malachite green were prepared by dissolving 1.2 mg poly(malachite green) or 1.2 mg malachite green in 50 ml water. The stock solutions of ascorbic acid (2.0 mM) and dopamine (1.0 mM) were prepared by dissolving them in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution and then diluted with 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution to the required concentration before measurements.

### 2.2. Apparatus

Electrochemical experiments were conducted on a CHI 760B electrochemical workstation (CH Instruments, Austin, USA) with a conventional three-electrode system at constant room temperature (22 °C). The poly(malachite green) film coated glassy carbon electrode or a bare glassy carbon electrode 3 mm in diameter was employed as the working electrode. A twisted platinum wire and a Ag|AgCl (3 M KCl) were used as the auxiliary electrode and reference electrode, respectively. The potentials mentioned throughout this paper were against the above reference electrode. The anodic current is positive and the cathodic one is negative.

The FT-IR spectra were recorded on a Protege 460 FT-IR spectroscope (Nicolet, Japan) and the UV–vis spectroscopy was performed on a UV-570 spectrometer (JASCO, Japan) and a 10-ml crystal cell was used. A pH 3C meter (Shanghai, China) was used for the adjustment of pH values of solutions and an ultrasonic bath (Kunshan, China) for cleaning electrodes and preparation of samples.

### 2.3. Electrosynthesis of poly(malachite green) films on glassy carbon electrodes

Prior to electropolymerizing of malachite green, the glassy carbon electrode was polished consecutively with 0.3 and 0.05 μm alumina slurries on a polishing cloth, washed continuously with 2.0 M NaOH, 1:1 $HNO_3$, and deionized water in a 5-min period for each cleaning solution in the ultrasonic cleaner. The cleaned glassy carbon electrode will have a mirror-like surface and it was then electroactivated in 0.1 M sulfuric acid *via* cycling within the potential range from −1.0 to 2.0 V at a scan rate of 100 mV $s^{-1}$ until a repeatable voltammogram was obtained. Electropolymerization of malachite green was conducted on the resulting glassy carbon electrode through scanning at a sweep rate of 100 mV $s^{-1}$ in a 10 mM malachite green aqueous solution containing 0.5 M $NaNO_3$ and 0.025 M $K_2HPO_4$–$KH_2PO_4$ (pH 6) buffer solution from −1.4 to 1.8 V for 20 cycles. After rinsing the electrodes copiously with water, the poly(malachite green) film coated glassy carbon electrode was fabricated. The thickness of poly(malachite green) films was altered by changing the scan cycles.

### 2.4. Optical characterization of poly(malachite green) film coated electrodes

The FT-IR spectra of poly(malachite green) films and of the monomer of poly(malachite green), malachite green, were recorded using KBr pellets. The KBr pellet of poly(malachite green) was prepared as follows: poly(malachite green) film was stripped carefully from the glassy carbon electrode's surface. Poly(malachite green) powder (1.2 mg) was weighed, mixed with crystal KBr powder in a mortar, and fabricated as one pellet. To compare the FT-IR spectrum of poly(malachite green) with that of malachite green quantitatively, the same amount (1.2 mg) of malachite green was used for the preparation of malachite green pellet in the same manner as prepared for poly(malachite green). The UV–vis spectra of poly(malachite green) and malachite green were obtained from their aqueous solutions in the same concentration and the background was automatically subtracted.

### 2.5. Voltammetric responses of poly(malachite green) film coated electrodes

Voltammetric responses of poly(malachite green) film coated glassy carbon electrode were obtained in different electrolyte solutions at required scan rates. The investigated solutions included sulfuric acid, $KNO_3$, $K_2HPO_4$, $KClO_4$, $KNO_3$, $KH_2PO_4$, LiCl, NaCl, KCl, $NH_4Cl$ solutions, and $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution in the absence/presence of ascorbic acid and/or dopamine. The chronocoulometric curves of the poly(malachite green) film coated glassy carbon electrode were recorded in 0.1 M $H_2SO_4$ and the potential was stepped from 0.5 to −0.1 V with an initial potential of 0.5 V and held at 0.5 V for 0.5 s. Electrochemical impedance spectroscopy was conducted in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution in the frequency range of 0.1–$10^5$ Hz. The DC voltage and AC amplitude were 0.5 V and 4 mV, respectively.

### 2.6. Sample treatment and analysis

Vitamin C tablets (0.274 g, Xiangfan Pharmaceutical Co., Xiangfan, China) were weighed, dissolved in 50 ml water, and kept in the fridge for 12 h. Then 5 ml transparent supernatant was diluted with 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution to 50 ml which served as samples for the detection of ascorbic acid in the tablets. The samples of dopamine were prepared from dopamine injections (20 mg dopamine in 2 ml solution, Jiangshu Jinyun Pharmaceutical Co., Jiangshu, China) which were diluted directly with 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution to 250 ml. The samples of ascorbic acid and dopamine were prepared by mixing the two resulting samples with a volume ratio of 1:1.

Before measuring the content of ascorbic acid and dopamine in samples, the working curves (the plots of the anodic peak current *vs.* the concentration) were drawn based on the first derivative of the voltammograms obtained from the stock solutions of ascorbic acid and dopamine in different concentrations and the scan rate used was 50 mV $s^{-1}$. The voltammograms of samples were then recorded and the anodic peak currents for ascorbic acid and dopamine were then measured. Using their working curves the contents of ascorbic acid and dopamine were estimated.

## 3. Results and discussion

Fig. 2 shows cyclic voltammograms of electropolymerization of malachite green on the glassy carbon electrode from 10 mM malachite green dissolved in 0.5 M $NaNO_3$ and 0.025 M $K_2HPO_4$–$KH_2PO_4$ (pH 6) buffer solution. One obvious anodic wave at 0.8 V and two cathodic waves at −0.4 and −1.2 V were noticed. The anodic current kept increasing from 0.9 to 1.8 V. The peak currents of these waves enlarged with increased cycling numbers although with a little shift of peak potentials. After 10 cycles, a transparent and colorful film was found to form on the electrode surface. Similar phenomena (colorful films formed on the electrode surface during the polymer polymerization process) have been noticed when methyl red [35], bromocresol green [36], and alizarin red [37]

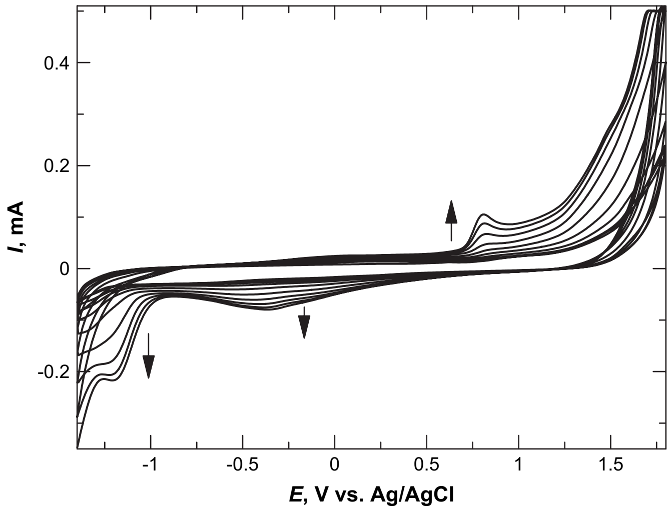

Fig. 2. Cyclic voltammograms of polymerization of malachite green on the glassy carbon electrode in the potential range from −1.4 to 1.8 V at a scan rate of 100 mV $s^{-1}$. The polymerization solution was 10 mM malachite green aqueous solution containing 0.5 M $NaNO_3$ and 0.025 M $K_2HPO_4$–$KH_2PO_4$ (pH 6) buffer solution. The cycling number was 20.

were polymerized potentiodynamically on the glassy carbon electrode. Although it is still unclear for us about the possible mechanism and reasonable reason which cause the polymer films' color until now, these facts indicate the polymerization of malachite green on the glassy electrode surface. The shift of peak potential is then possibly related to the resistance change of the poly(malachite green) film.

In order to confirm the formation of poly(malachite green) on the glassy carbon electrode, FT-IR and UV–vis spectra of the resulted transparent and colorful film and of malachite green were recorded. Fig. 3 shows the FT-IR spectra of malachite green (curve a) and the resulted film (curve b). Curve (a) and curve (b) both show strong absorption bands at 2918.13 $cm^{-1}$, 2855.96 $cm^{-1}$, 1183.42 $cm^{-1}$ and the intensities of these bands of the resulted film in curve (b) are stronger than those of malachite green in curve (a). The absorptions at 2918.13 $cm^{-1}$ and 2855.96 $cm^{-1}$ obviously resulted from the $-CH_3$ groups. Curve (b) shows a new band at around 3421.76 $cm^{-1}$ possibly resulting from −OH. Another new band at 1388.60 $cm^{-1}$ is possibly caused by the conjugated double bonds in the poly(malachite green) film. These increased intensities of the methyl and conjugated double bonds in the FT-IR spectra suggest an increase of these functional groups, namely, the polymerization of malachite green. The appearance of the band of −OH indicates that the solvent (water) is incorporated into the film. In addition, the UV–vis spectrum (not shown) of the resulted film showed a band at 730.50 nm while that of malachite green did at 620 nm, an indication of formation of the quinoid structure in poly(malachite green). Spectroscopic and electrochemical results confirm the formation of poly(malachite green) film on the glassy carbon electrode. According to these results the possible polymerization mechanism of malachite green on the glassy carbon electrode was then suggested and schematized in Fig. 4.

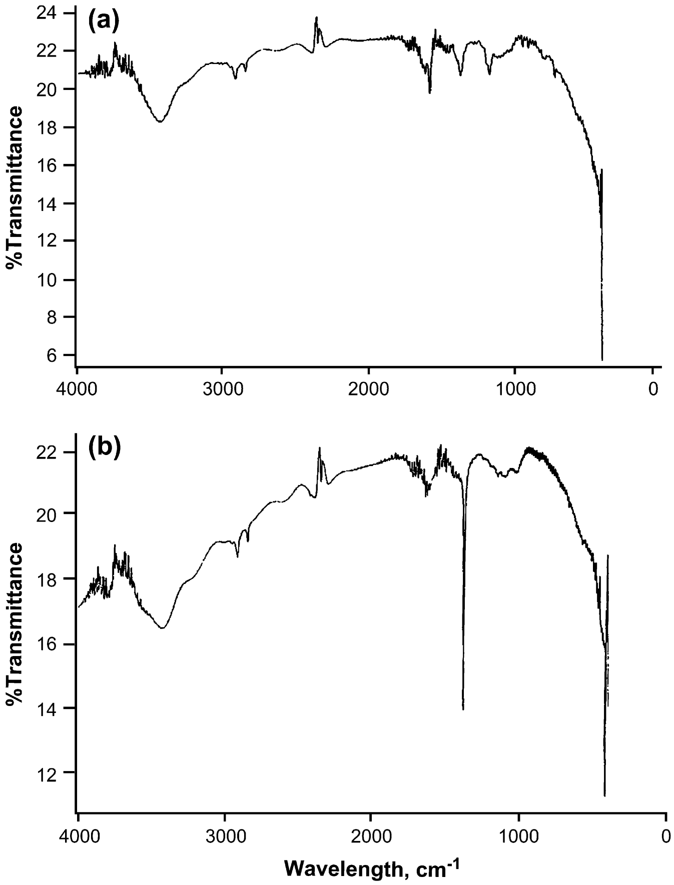

Fig. 3. FT-IR spectra of malachite green (curve a) and of poly(malachite green) (curve b). The same amount of malachite green and poly(malachite green) was used to prepare their pellets.

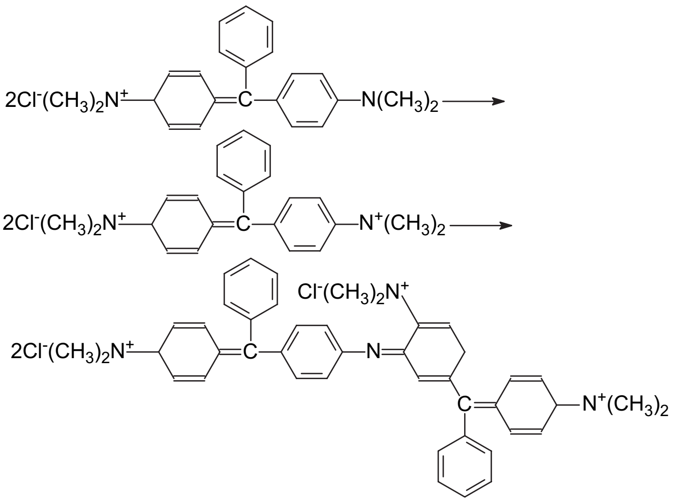

Fig. 4. The possible growth mechanism of poly(malachite green) on the glassy carbon electrode from 10 mM malachite green dissolving in 0.5 M $NaNO_3$ and 0.025 M $K_2HPO_4$–$KH_2PO_4$ (pH 6) buffer solution.

Electrochemical activity (redox behavior) of the as-prepared poly(malachite green) film on the glassy carbon electrode was then investigated in 0.1 M $H_2SO_4$ at various scan rates and in $K_2HPO_4$–$KH_2PO_4$ buffer solution with different pH values. Fig. 5 shows cyclic voltammograms of

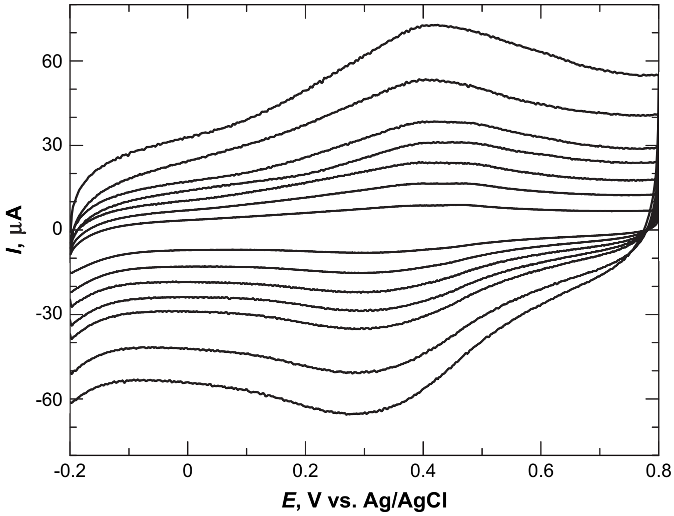

Fig. 5. Cyclic voltammograms of the poly(malachite green) film coated glassy carbon electrode in 0.1 M $H_2SO_4$ solution at various scan rates. From inner to outer the scan rate was 10, 20, 40, 60, 80, 100, and 150 mV $s^{-1}$.

the poly(malachite green) film coated glassy carbon electrode in 0.1 M $H_2SO_4$ in the potential range of $-0.2$ to 0.6 V at various scan rates ranging from 10 to 150 mV $s^{-1}$. One couple of redox waves appeared at potentials of around 0.42 and 0.31 V for the anodic peak and cathodic one, respectively. The peak potentials did not alter with increased scan rates while both of the peak currents enhanced proportionally with scan rates. The net charge for the anodic wave estimated *via* the integration of the anodic wave was almost equal to that for the cathodic one at different scan rates. These waves suggest that poly(malachite green) is a redox polymer and its redox reaction possibly results from the quinoid structure inside it, as demonstrated previously. The independence of peak potentials on scan rates together with the linear variation of peak current against scan rates demonstrates that the redox reaction is a reversal process controlled by adsorption. Provided that the redox reaction of one quinoid in poly(malachite green) film involves two electrons ($n = 2$), the surface coverage ($\Gamma$) of poly(malachite green) film on the glassy carbon electrode was then evaluated to be 0.49 μmol $m^{-2}$ according to the expression $\Gamma = Q/nFA$ [38] where $Q$, $A$, and $F$ are the net charge of anodic wave (or cathodic one) after being subtracted from the charge caused by the capacitive/charging current, the real surface area of the glassy carbon electrode (0.13 $cm^2$) [35], and Faraday constant, respectively. Moreover, the thickness of poly(malachite green) film on the glassy carbon electrode ($l$) is possible to be estimated according to the equation $l = QM/\rho AnF$ [38], where $M$ and $\rho$ are, respectively, the molecular weight and the density of poly(malachite green) and other terms have the same meanings as described above. However, we failed in obtaining the thickness of poly(malachite green) film since the values of $M$ and $\rho$ are not available (detectable) in our experiments. However, the surface coverage of polymer films and cycling numbers used in the electrosynthesis of polymer are always adopted to describe the thickness of polymer films in the literature since the thickness of the conducting polymer films is enhanced proportionally to the net charge cost for polymerization, namely, to cycling numbers when the potentiodynamic mode is employed to generate conducting polymer films on the electrode [9,10]. Throughout this paper cycling numbers were utilized for the description of the thickness of poly(malachite green) films and 20 cycles were used for the fabrication of poly(malachite green) film on the glassy carbon electrode. The equal net charge of the cathodic wave to that of the anodic one indicates similar conductivity of poly(malachite green) films in oxidation state with that in reduction state. Its conductivity expressed in terms of capacitance will be detected using electrochemical impedance spectroscopy in the later section.

Fig. 6 shows cyclic voltammograms of the poly(malachite green) film coated electrode with different pH values ranging from 2.1 to 6.1 at a scan rate of 40 mV $s^{-1}$. The shape of voltammograms obtained in $K_2HPO_4-KH_2PO_4$ buffer solution was much worse than those obtained in 0.1 M sulfuric acid, as shown in Fig. 5 and the currents were close to each other at the same scan rate. The anodic peak potential shifted negatively while the peak current decreased with an increase in pH values. The peak potentials of anodic and cathodic waves *vs.* pH values showed linear lines in the pH value ranging 2.1–6.1 with absolute values of the slopes of 58 mV $pH^{-1}$, which implies the participation of one proton during redox reaction of poly(malachite green) films [38]. The decreased peak current results from a decade of the concentration of proton in the solutions. These facts confirmed the existence of quinoid structures in poly(malachite green) films which agrees with the results obtained from voltammetric investigations and proves the growth mechanism of poly(malachite green) on the glassy carbon electrode, as shown in Fig. 4.

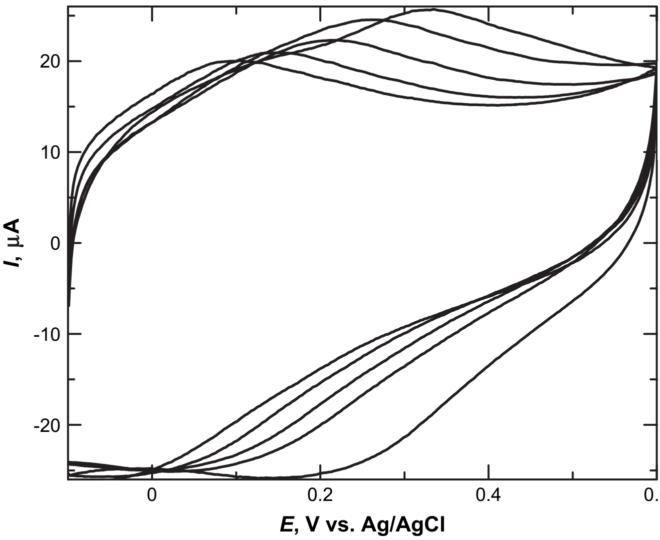

Fig. 6. Cyclic voltammograms of the poly(malachite green) film coated glassy carbon electrode at a scan rate of 40 mV $s^{-1}$ in $K_2HPO_4-KH_2PO_4$ buffer solution with various pH values ranging from 2.1 to 6.1. From right side to left side the pH values were 2.1, 3.5, 4.1, 5.1, and 6.1.

Chronocoulometry of the poly(malachite green) film coated glassy carbon electrode was performed in 0.1 M sulfuric acid with an aim to determine the charge (protons) transfer coefficient in poly(malachite green) films. Fig. 7 shows the chronocoulometric curve of poly(malachite green) film with a step potential from 0.5 to $-0.1$ V and an initial potential of 0.5 V. The charge increased quickly with time and reached a plateau after 20 ms. A linear line of the charge as a function of square root of time derived from the chronocoulometric curve was obtained with a slope of 0.14 mC $s^{-1/2}$. Assuming that the charge (proton) transfer in the poly(malachite green) film fit half-infinite diffusion, the diffusion coefficient of charge transfer (the movement of $H^+$) was calculated [38,39] to be $7.5 \times 10^{-5}$ $cm^2$ $s^{-1}$, which is almost eight times larger than the diffusion coefficient of usual molecules ($1.0 \times 10^{-5}$ $cm^2$ $s^{-1}$). This suggests that the permeation of $H^+$ through poly(malachite green) films is in a high speed. These results are in accordance with the good electrochemical activity exhibited as voltammetric response of poly(malachite green) films. Similar fast charge (protons) transport has also been observed for the poly(methyl red) film [35]. In contrast, charge (proton) transport of polypyrrole [9,10] is at a slower rate. These discrepancies may be due to the different structures of these polymers, e.g., polypyrrole has a cross-linked and

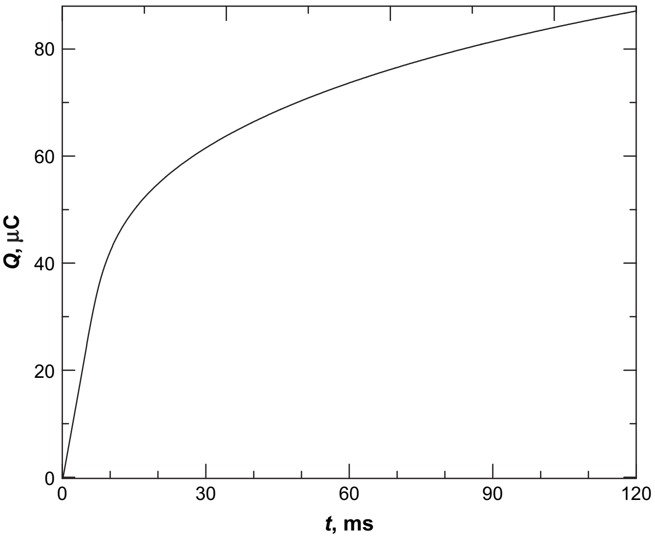

Fig. 7. Chronocoulometric curves of poly(malachite green) film coated glassy carbon electrode in 0.1 M $H_2SO_4$ solution. The step potential was from 0.5 to −0.1 V and the initial potential was 0.5 V and kept for 0.5 s.

closed structure while poly(malachite green) has a non-cross-linked and open one.

In an effort to demonstrate the conductivity of poly(malachite green) films, the resistance of poly(malachite green) films expressed by capacitance was determined by electrochemical impedance spectroscopy in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution. The Nyquist curve (solid line) and the Randles curve (dashed line) re-plotted from the Nyquist curves are shown in Fig. 8. In the high frequency area, the time for the semi-periodic extension was short, indicating no changes in the surface concentration of electroactive species. Namely, no diffusion layer exists or it is a non-diffusion process. In contrast, in the low frequency area a linear line with an angle of 45° was shown. This is Warberg diffusion area where the electrochemical process is controlled by the diffusion of electroactive species. Thicker poly(malachite green) films were found to slow down this kind of conversion from a non-diffusion process into a diffusion one. This may be due to the increased resistance of the poly(malachite green) film with its thickness. The capacitance ($C_{dl}$) of poly(malachite green) film was then estimated from the Randles curve (dashed line) [38] to be 25 $\mu F\,cm^{-2}$, which is close to that of a bare gold electrode (20 $\mu F\,cm^{-2}$). The almost similar conductivity of poly(malachite green) with bare a gold electrode demonstrates that poly(malachite green) film is metallic or an electronically conductive polymer [9]. This can also be supported by its electrochemical activity and fast charge (proton) transfer speed of poly(malachite green) film in sulfuric acid.

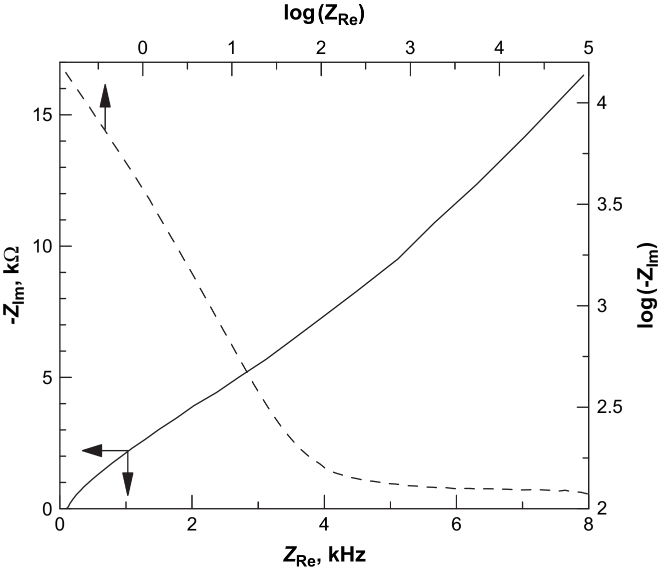

Fig. 8. The Nyquist plot (solid line) of the poly(malachite green) film coated electrode in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution in the frequency range of 0.1–$10^5$ Hz and the resulted Randle plot (dashed line) of [log($-Z_{Im}$)] as a function of [log($Z_{Re}$)] re-plotted from the Nyquist plot. The DC voltage and AC amplitude were 0.5 V and 4 mV, respectively.

Since poly(malachite green) film is electronically conductive, anion and/cation will be injected/ejected during their redox cycling in supporting electrolyte. Ion transport of poly(malachite green) films was thus investigated in various supporting electrolytes in the potential range of −0.2 to +0.65 V at a scan rate of 40 $mV\,s^{-1}$. Two types of supporting electrolytes were chosen: one having same cation but different anions ($KNO_3$, $KH_2PO_4$, and $KClO_4$), another having same anion but different cations (HCl, LiCl, NaCl, KCl, and $NH_4Cl$). Cyclic voltammograms of poly(malachite green) film coated glassy carbon electrode exhibited different behaviors in the different supporting electrolyte (not shown). An increase in the concentration of supporting electrolyte resulted in the positive shift of the anodic wave and the cathodic peak potential shifted negatively with a decrease in the concentration of supporting electrolyte. This tendency is in agreement with the results reported in Ref. [40]. On the other hand, the maximum current was reached in HCl buffer while cyclic voltammogram in $NH_4Cl$ solution gave smaller current and ugly voltammetric shape. The diameter of ions was also found to affect the current and the shape of voltammograms. Larger diameter of anions made the anodic peak potentials shift negatively but the cathodic peak potential positively. Although the amount of ejected/injected ions is hard to be predicted from current experiment, these facts suggest that anion incorporation and/or cation ejection occurred during redox cycling of poly(malachite green) film. Since poly(malachite green) films were prepared in potentiodynamic mode, the poly(malachite green) is actually in the mixed reduction/oxidation state which is quite different from that of the film generated using potentiostatic mode (where the film stays only in oxidation or reduction state), and hence cation/anion injection/ejection was observed. Consequently, poly(malachite green) is an electronically conducting polymer and has redox ability.

Since poly(malachite green) film is electronically conductive and showed a high speed of charge transfer during redox reaction, it is promising to be utilized as a catalytic layer for the oxidation of bio-molecules like ascorbic acid and dopamine. Fig. 9 shows cyclic voltammogram of 1.0 mM ascorbic acid on the poly(malachite green) film coated electrode (curve

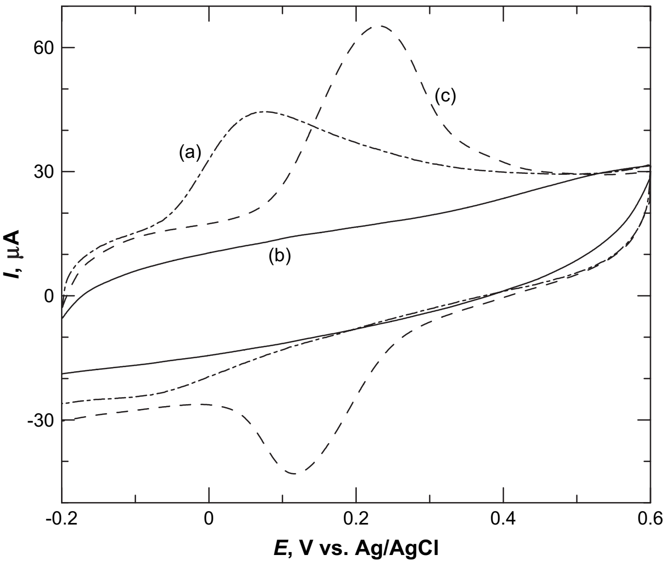

Fig. 9. Cyclic voltammograms of 1.0 mM ascorbic acid (curve a, dashed-dotted line) and 0.5 mM dopamine (curve c, dashed line) on the poly(malachite green) film coated glassy carbon electrode in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution. Curve (b) (solid line) is the voltammogram of the poly(malachite green) film coated electrode in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution. The scan rate was 40 mV $s^{-1}$.

a) in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution. The voltammogram of ascorbic acid shows one anodic wave at 0.07 V, 230 mV negative than the oxidation of ascorbic acid (0.30 V) on the bare glassy carbon electrode (not shown) and the magnitude of corresponding peak current was much smaller than that on the poly(malachite green) film coated glassy carbon electrode. The voltammogram of the poly(malachite green) film coated electrode (curve b) in the blank solution without ascorbic acid or dopamine is featureless. The peak potential of ascorbic acid on the poly(malachite green) film coated electrode was noticed to shift positively with scan rate and its peak current was proportional to scan rate in the range of 5–200 mV $s^{-1}$. The negative shift of peak potential and enhanced peak currents of ascorbic acid on the poly(malachite green) film coated glassy carbon electrode suggest that the anodic wave at 0.07 V is caused by the catalysis of poly(malachite green) towards the oxidation of ascorbic acid. This process is irreversible and controlled by adsorption.

Meanwhile, Fig. 9 shows the voltammogram of 0.5 mM dopamine (curve c) on the poly(malachite green) film coated glassy carbon electrode in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution, in which a couple of waves at 0.28 and 0.11 V for the anodic and cathodic waves, respectively, is exhibited. The anodic peak current of dopamine on the poly(malachite green) film coated electrode was equal to the cathodic one and proportional to the square root of scan rate in the range of 5–200 mV $s^{-1}$. The anodic peak potential shifted positively with increased scan rates while the cathodic one did negatively. These results indicate that the oxidation of dopamine on the poly(malachite green) film coated electrode at 0.28 V is a diffusion-controlled quasi-reversible process and the cathodic wave at 0.11 V is due to the reduction of the oxidized dopamine on the modified electrode. In contrast, the oxidation of dopamine on the bare glassy carbon electrode occurred at 0.66 V (not shown), 380 mV positive than that on the poly(malachite green) film coated glassy carbon electrode. The resulting peak current on the bare glassy carbon electrode was also smaller than that on the poly(malachite green) film modified glassy carbon electrode. Therefore the poly(malachite green) film coated electrode also has the catalytic ability towards dopamine. The difference in mass transfer process of ascorbic acid (adsorption-controlled) from that of dopamine (diffusion-controlled) on the poly(malachite green) film coated glassy carbon electrode is presumably due to the ionized structure of poly(malachite green) and the charge state of ascorbic acid (negative charges) and dopamine (neutrality). In other words, the poly(malachite green) polymerized film in the potentiodynamic mode is favorable to adsorb negative charges since it itself has positive charge groups inside as shown in Fig. 4. The catalytic ability of poly(malachite green) towards ascorbic acid and dopamine is reasonable to originate from the multi-electroactive spots (quinoid structure) inside polymers and big surface area (due to porous structure) of polymers in the similar catalytic way as other reported polymers did [9,16,27–37].

Dopamine is always accompanied with ascorbic acid, voltammetric response of the mixture of ascorbic acid and dopamine on the poly(malachite green) film coated glassy carbon electrode was thus recorded and presented in Fig. 10. The voltammogram shows two anodic waves at 0.1 and 0.28 V and one cathodic wave at 0.16 V and these waves have been assigned previously to the oxidation of ascorbic acid and dopamine and to the reduction of the oxidized dopamine, respectively. The current response of ascorbic acid was weaker than that of dopamine, in agreement with cyclic voltammograms in Fig. 9. The separation of the anodic peak potential of ascorbic acid with that of dopamine was 180 mV and therefore the

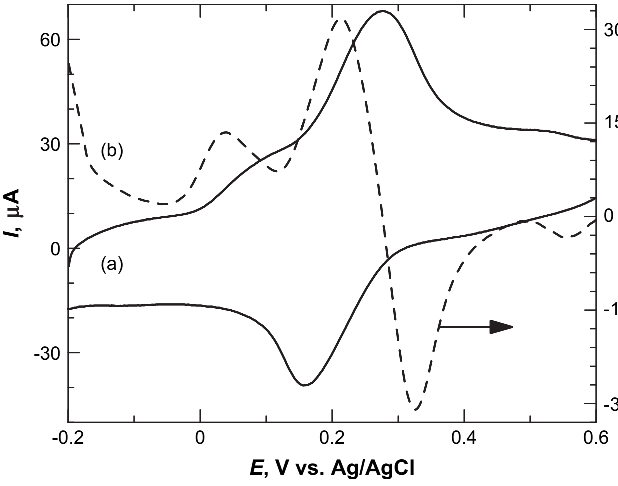

Fig. 10. Cyclic voltammogram (curve a, solid line) and the first derivative of the voltammogram (curve b, dashed line) of 1.0 mM ascorbic acid and 0.5 mM dopamine in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution on the poly(malachite green) film coated glassy carbon electrode at a scan rate of 40 mV $s^{-1}$.

poly(malachite green) film coated glassy carbon electrode can be applied for the simultaneous detection of ascorbic acid and dopamine. In order to enhance the signal of ascorbic acid and dopamine, the first derivation of the voltammogram was drawn from curve (a) and shown as curve (b) in Fig. 10 where the current responses were much enhanced compared with those of ascorbic acid and dopamine in curve (a). The peak currents in the first derivation of cyclic voltammogram of ascorbic acid and dopamine on the poly(malachite green) film coated glassy carbon electrode were linear with their concentration. The linear regression equations for ascorbic acid and dopamine were, respectively, $I_{\mathrm{p,AA}} = -0.0321c_{\mathrm{AA}} - 2 \times 10^{-5}$ in the concentration range of 0.5 μM–10 mM and $I_{\mathrm{p,DA}} = -0.064c_{\mathrm{DA}} - 2 \times 10^{-5}$ in the concentration range of 10 mM–0.1 μM where $I_{\mathrm{p,AA}}$, $I_{\mathrm{p,DA}}$, $c_{\mathrm{AA}}$, and $c_{\mathrm{DA}}$ are the peak current of ascorbic acid, peak current of dopamine, concentration of ascorbic acid, and concentration of dopamine, respectively. The detection limits according to the IUPAC recommendation were 160 nM and 30 nM for ascorbic acid and dopamine, respectively.

Based on the above calibration curves for ascorbic acid and dopamine, the content of ascorbic acid and dopamine in vitamin pills and dopamine injections was determined separately and simultaneously. The treatment and preparation of samples were described in Section 2. The average content of ascorbic acid in each of Vitamin C tablets for five times was detected to be 0.739 g and the RSD for these measurements was 1.39%. The average content of dopamine in dopamine injection for 10 times was monitored to be 10.45 mg $\mathrm{ml}^{-1}$ and the RSD for these detections was 1.62%. The average concentration of ascorbic acid and dopamine in the mixed samples was 0.04 g and 2.03 mg $\mathrm{ml}^{-1}$, respectively, and the RSD was 1.71%. The determined value agrees well with the standard values provided by the company using optical method. The reproducibility was detected by monitoring 1.0 mM ascorbic acid and 0.1 mM dopamine for 10 times and the corresponding RSD was 1.84 and 2.51% for ascorbic acid and dopamine, respectively. The stability of poly(malachite green) film coated glassy carbon electrode was also checked by recording voltammetric response of 1.0 mM ascorbic acid and 0.5 mM dopamine in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution. The poly(malachite green) film coated electrode is so stable to be used for detection of ascorbic acid and dopamine for 15 days. Note here that after measurements it is always good to store the poly(malachite green) film modified glassy carbon electrode in water or 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution and before each measurement it is better to refresh the modified electrode in 0.5 M $K_2HPO_4$–$KH_2PO_4$ (pH 7.4) buffer solution to remove the adsorbed ascorbic acid and dopamine of the previous measurements. The poly(malachite green) film coated glassy carbon electrode also showed a good selectivity towards ascorbic acid and dopamine. Several species that frequently existed with them in pharmaceutical and injections were inspected by measuring voltammetric response of their mixtures. The presence of epinephrine, norepinephrine, and uric acid will influence the detection of ascorbic acid and dopamine on the poly(malachite green) film coated electrode and the possible ways to remove their interference is currently under research. However, no interferences were found when other water soluble vitamins (e.g. thiamine, riboflavin, pyridoxine, nicotinamide, nicotic acid, folic acid were present). Some other possible interference of vitamins like retinol palmitate and tocopherol acetate did not affect the detection at all due to their insoluble property in aqueous solutions. Therefore, poly(malachite green) film coated electrodes are practically possible to be employed as an electrochemical sensor for the monitoring of ascorbic acid and dopamine separately in pharmaceutical, clinic, food, and biochemical liquid samples.

## 4. Conclusion

An electronically conducting polymer, poly(malachite green), has been synthesized electrochemically from malachite green on the glassy carbon in potentiodynamic mode. The existence of quinoid structure was rationalized by optical and electrochemical techniques. Poly(malachite green) film shows a high speed of charge (proton) transfer and anion/cation injection/ejection behavior during their redox cycling. The conductivity of as-prepared poly(malachite green) film was also obtained from its electrochemical impedance spectroscopy in terms of capacitance of the film. Owing to quinoid structure inside the polymer and large surface area of poly(malachite green), the poly(malachite green) film coated glassy carbon electrode exhibited excellent catalytic ability towards ascorbic acid and dopamine and the detailed catalytic kinetic will be investigated sufficiently in a forthcoming paper. The oxidation of ascorbic acid was separated, 180 mV, from that of dopamine on the poly(malachite green) film coated glassy carbon electrode and the catalytic currents were linear with their concentration in a wide concentration range. Voltammetric detection of ascorbic acid and dopamine separately and simultaneously was successfully conducted on poly(malachite green) film modified glassy carbon electrodes. Poly(malachite green) film coated electrode will have the potential to be utilized as an electrochemical sensor for monitoring of ascorbic acid and dopamine in pharmaceutical, clinic, food, and biochemical liquid samples in future.

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