

Electrochemical Syntheses and Characterization of Some Polydyes and their Application for the Simultaneous Determination of Ascorbic Acid and Uric Acid

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Abstract

The electropolymerization and characterization of the monomers: gentian violet (GV), brilliant green (BG), aniline, and methyl violet (MV) and their copolymers were done using cyclic voltammetry (CV) on glassy carbon electrode (GCE) as a working electrode against Ag/AgCl reference electrode and platinum wire as counter electrode. The copolymers showed higher current peaks than their corresponding homopolymers. The electrochemical characterization of these polymers and copolymers was studied by scan rate effect each between 10 and 300 mV/s and pH effect between 1.56 and 5.30. After being modified by the copolymers: poly(BG-GV) and poly(BG-MV), the modified GCE showed good results in resolving the peaks of ascorbic acid and uric acid which otherwise showed one broad peak on bare GCE. The determination of the area of the modified electrode was done with all polymers investigated and also their copolymers. The CV in bare GCE was scanned at different scan rates of 4 mM $K_3[Fe(CN)_6]$ in 1 M KNO_3 solution. The square root of scan rate dependence of peak current was plotted and the Randles-Sevcik equation was applied to determine the diffusion coefficient of $Fe(CN)_6^{3-}$ ion and which was $1.13 \times 10^{-14} \text{ cm}^2/\text{s}$. This was used to determine the area after running the CV of 4 mM $K_3[Fe(CN)_6]$ in 1 M KNO_3 at different scan rates. From the plot of peak current vs. square root of scan rate, the slope was determined and used to determine the area of the modified electrode from the Randles-Sevcik equation.

1. Introduction

Conducting polymers have much interest among researchers due to their special characteristics such as their ability to conduct electricity, they are stable, simplicity for preparation, inexpensiveness, and redox properties compared to other organic compounds. Because of their conductivity properties, they have been used in sensors, electromagnetic shielding, photovoltaic cells, and organic light-emitting diodes [1].

The color of the dyes is due to: 1) their absorption of light in the visible spectrum (380–700 nm), 2) the presence of chromophore(s), 3) the conjugation, i.e. a structure with alternating double and single bonds, and 4) the resonance of electrons, which is a stabilizing force in organic compounds. Gentian Violet (GV), Brilliant Green (BG), and Methyl Violet (MV) are organic dyes that belong to the family of triphenylmethanes (triphenylmethanes are dye compounds and the fact that they have an open, ionized structure is promising for fast charge transfer and for catalytic ability in ionic transport) [2–8].

In this work, electropolymerizations of GV, BG, and MV have been made to modify the GC electrode. The modified electrodes were used for sensing uric acid and ascorbic acid mixture.

2. EXPERIMENTAL

2.1. Apparatus and Chemicals

GV, BG, and MV are analytical-grade reagents and were used without further purification. Aniline (Aldrich) was distilled before use for further purification.

Sulfuric acid (H_2SO_4) (Riedel-de Haen) 0.1 M was prepared and used as supporting electrolyte, hydrochloric acid (HCl) (BDH) 1 M was prepared in 100 mL volumetric flask and used in pH adjusting, sodium hydroxide (NaOH) (BDH) 1 M in 100 mL was prepared and used to adjust the pH, dipotassium orthophosphate (K_2HPO_4) (Fluka) used as phosphate buffer (PBS) different concentrations were prepared and used, potassium dihydrogen orthophosphate (KH_2PO_4) (Fluka) as PBS, disodium orthophosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) (BDH) as PBS, potassium nitrate (KNO_3) (BDH) 1 M was prepared and used in the preparation of potassium hexacyanoferrate, potassium hexacyanoferrate ($\text{K}_3[\text{Fe}(\text{CN})_6]$) (Merck) 4 mM, sodium sulphate (Riedel-de Haen) (Na_2SO_4) 0.5 M, uric acid and ascorbic acid were also used without special treatment.

2.2. Instrumentation

The electrochemical experiments were carried out in a three-electrode system containing Ag/AgCl as a reference electrode, platinum wire as a counter electrode and bare glassy carbon electrode (BGCE) or modified glassy carbon electrode as a working electrode at room temperature. All the electrochemical experiments were carried out using a computerized electrochemical analyzer (BAS CV-50W) which was connected to a Dell Pentium personal computer. The pH of the solutions was measured with a pH meter (model pH 211 Microprocessor pH meter) at room temperature.

2.3. Procedure

The GCE was first carefully polished with sandpaper and 0.05- μm alumina powder to produce a mirror-like surface and finally rinsed with distilled water. The solutions were prepared in distilled water.

All electrochemical polymerizations except polyaniline (PANI), which was electropolymerized by six cycles, were electropolymerized by fifteen cycles on CV and their corresponding films were created on the surface of the electrode. After they were produced on the electrode surface, the characteristics of the so modified electrode were studied at different scan rates of 10, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, and 300 mV/s in 0.1 M H_2SO_4 supporting electrolyte solution and also in 0.5 M Na_2SO_4 supporting electrolyte solution with different pH values: 1.56, 2.32, 3.35, 4.07, and 5.30.

3. Results and Discussion

3.1. Electropolymerization of Dyes (Gentian Violet, Brilliant Green, Aniline, and Methyl Violet)

Electrochemical polymerization of gentian violet at the glassy carbon electrode was done by using a cyclic voltammetric method in an aqueous solution that contains 2 mM of gentian violet in 0.2 M PBS (pH 5.8) and 0.1 M Na_2SO_4 . Electropolymerisation was achieved by the formation of film that grew between the potential ranges of -1,500 to 2,500 mV at a scan rate of 100 mV/s for 15 cycles using cyclic voltammetry (Fig. (a)).

The voltammogram of GV on GCE showed one peak on anodic scanning with no corresponding peak on the reverse scan. The appearance of a single anodic peak in the first cycle only, with no cathodic peak on the reverse scan, is indicative of the irreversible nature of the oxidation process. On progressive cycle, the anodic peak at 1,500 mV and the cathodic peak at around - 400 mV both increased with the number of cycles. This shows polymer growth on the electrode [8].

Polymerizing BG on GCE gives a continuous increase of the corresponding polymer peaks at around + 150, +800, -300 and - 1,400 mV, indicating that BG is electropolymerised up to the last cycle since GCE provides a more open structure for the passage of the monomer, thicker films of PBG being achieved as observed in Fig. 1. (b). At high positive potentials, ~+800 mV, irreversible monomer oxidation occurs. The redox couple at the potentials + 150 mV (oxidation peak) is due to the oxidation of brilliant green monomer and - 300 mV (reduction peak) is because of the reduction of the poly(brilliant green) (PBG) film formed at the surface of the GCE and in both cases, the height of the peaks increase with potential cycle, showing PBG growth [11, 12].

The polymerization of methyl violet takes place when the potential reaches about 1700 mV vs. Ag/AgCl. The growth of the polymer on the electrode can be seen in the increase of all the peaks, and it is more evident at the reduction one. As can be seen from Fig. 1 (c), an irreversible anodic peak with a peak potential of 1,750 mV vs. Ag/AgCl is found for MV oxidation on GCE. This result confirms that MV can be directly oxidized on GCE.

A couple of reversible (oxidation/reduction) peak is observed between the potential range of -400 mV and 250 mV. The height of this reversible peak increased successively with increasing potential cycles, indicating the formation of the polymer. The cathodic peak current of the polymer increases rapidly and its peak potentials shift a little towards a more negative potential with increasing the number of potential cycles while its anodic peaks remain nearly constant. This reason is that the film thickness of the poly(methyl violet) on the glassy carbon electrode was gradually growing during the electrolysis and caused a potential drop [16, 17].

In the electrodeposition of polyaniline in Fig. s1, the GC electrode proceeds via a radical cation mechanism. From the first cycle, there is only one anodic and one cathodic peak and up on cycling (cycles 2–7) three anodic and three cathodic peaks appeared at the potentials of 260 mV, 520 mV, and 770 mV (anodic peaks) and 16 mV, 370 mV, and 570 mV (cathodic peaks). As the number of cycles increases, the peak currents of these peaks increase. The peak at 260 mV indicates the transformation of the reduced leucoemeraldine salt form into the emeraldine salt form i.e., the electron transfer from the PANI film; the peak at 770 mV is assigned to the further oxidation into the pernigraniline form. The middle peak was assigned to the presence of cross-linking of PANI caused by the reaction of nitrenium species being present as intermediates or to over-oxidation products. On the reverse scan, the cathodic peak at 16 mV represents the electron transfer to the electrodeposited polyaniline film. The one at 570 mV probably corresponds to side reactions such as decomposition of the polymer.

The large currents observed at the positive end of the CV are due to the superposition of two distinct processes: one is the electron transfer from the PANI film corresponding to the oxidation of the PANI film and the other is the electron transfer from the aniline monomer to the electrode corresponding to the oxidation of the aniline monomer to produce a precursor for the PANI film [13–15].

The cyclic voltammetry curve of a deposited PANI film in monomer-free solution is shown in Fig. s1. The CV was scanned between the potential range – 200 and 1,200 V at a scan rate of 100 mV/s in a monomer-free 0.3 M H₂SO₄ solution. The first redox couple corresponds to the redox reaction between leucoemeraldine and emeraldine, and the third redox couple to the redox reaction between emeraldine and pernigraniline, respectively. The second redox process belongs most probably to some quinone or quinoneimine-type degradation products, formed during the electrochemical preparation of the polymers. In order to compensate for the charge of the PANI film, anion doping/dedoping of the polyaniline film occurs [2].

Besides the proton/cation exchange, the anion is also expelled from the polyaniline film during deprotonation [16–18].

3.1.1. Voltammetric characterization of GC/(PGV, PBG, and PMV) modified electrode

3.1.1.1. Scan rate effect

To study the electrode behavior, the scan rate for PGV was varied between 10 and 300 mV/s and the change in current response of 0.1 M H₂SO₄ was observed. The peak intensities (both the cathodic and the anodic) depend linearly on the scan rate, i.e., as the scan rate increases, the peak intensities also increase linearly.

As one can easily observe from Fig. 2, there is no shift of peak potential with the increment of the scan rate. This indicates that the redox reversal process is adsorption-controlled.

Figure s2 shows the relationship (the scan rate for PGV) between I_{pa}/I_{pc} and $v^{1/2}$ (mV/s)^{1/2}. Both anodic and cathodic peak currents depend linearly on the square root of the whole scan rate range examined, which suggested a diffusion-controlled process in solution [9, 10].

The slope of the curve I_{pa} versus $v^{1/2}$ is slightly greater than the corresponding reduction process, meaning that the oxidation process occurs with a higher electron transfer rate [11, 12].

Electrochemical activity (redox behavior) of the PBG film on the GCE was investigated in 0.1 M H₂SO₄ at various scan rates as observed in Fig. 2 (b). The peak intensities (both the cathodic and the anodic) depend linearly on the scan rate. Up on the increment of sweep rate, there is a little shift of peak potentials in both cathodic and anodic peak potentials, i.e. as the sweep rate increases, the anodic peak potentials shift to positive and that of the cathode shift toward more negative. This shifting is the

characteristic of multi-layer modified electrodes, where mass transfer is done through the film, and also of the processes with slow electron transfer or influenced by an ohmic drop effect. They all show a linear dependence of the peak current on the square root of the potential scan rate, so that the electrochemical process at the electrode is controlled by diffusion of the counterion.

Electrochemical activity (redox behavior) of the PMV film on the GCE was investigated in 0.1 M H₂SO₄ at various scan rates and the peak currents are observed in Fig. 2 (c). enhanced proportionally with scan rates imply a diffusion-controlled process and the peak potentials shifted toward positive and negative potentials for the anodic and cathodic peak potentials, respectively which is the characteristics of multi-layer modified electrodes, where a mass transfer is done through the film, and also of the processes with slow electron transfer or influenced by an ohmic drop effect.

3.1.1.2. Effect of solution pH

It has been found that when organic dye polymers are in solution or chemically adsorbed at electrode surfaces, they possess a midpoint potential which is highly pH-dependent. It was therefore necessary to investigate the variation of midpoint potential with pH for the electropolymerised dyes since this influences the applied potential [11].

The pH indicates the number of hydrogen ions in a solution. Since the solution pH has a significant effect on chemical reactions, the measurement and control of pH are very important. The effect of solution pH has a significant contribution to electrochemical oxidation and was carefully investigated by the CV technique. Its effect on the response of PGV-modified GCE was investigated in the range of pH 1.56–5.30 on the CV.

From Fig. 3 (a) both the anodic and cathodic peak potentials shifted toward negative and the current peaks decreased as pH values increased. Shift in the negative direction with a rising value of pH, suggesting that protons have participated in electrode reactions. The voltammogram also becomes more irreversible with the increment of the pH.

Figure s3 shows the peak potential dependence of the redox couple of PGV on the pH. The difference between both peaks is that the slope of the cathodic peak potential dependence (3.09 mV/pH) is roughly twice larger than the slope of the anodic one (1.45 mV/pH). This result points out the participation of two hydrogen ions in the electrochemical reaction associated with the cathodic peak and only one proton in the anodic one.

For the GCE coated with PBG film (Fig. 3 (b)), the peak potential moves to more negative potentials as pH increases, suggesting that a protonation, prior to the electron transfer, must occur in the reduction, as well as deprotonation in the oxidation. The peak width increases with pH. This means as pH increases the peak becomes more irreversible. The intensity of the peaks decreases as pH values increase and this is associated with a decrease of the hydrogen ion concentration.

From Fig. 3 (c) (the pH dependence voltammogram of PMV film coated GCE) as the pH value increases, there is a shift toward the negative potential from the potential of 250 mV for the smallest pH value (1.56) to 50 mV for the highest value of pH (5.30). Shift in the negative direction with a rising value of pH, suggesting that protons have participated in electrode reactions.

3.1.2. Electropolymerisation of Copolymers

Before electropolymerisation of the copolymers, the optimum mole ratio of the two dyes was determined from different mole ratios after scanning the mixtures of two dyes in the supporting electrolyte, as shown in Fig. 4.

The inset graphs show the comparison where the maximum peak current is produced for the mixtures of two dyes in each ratio. By this method the optimum ratio selected for the mixtures of (a) poly(gentian violet-brilliant green) is 1:3 (GV: BG), (b) poly(aniline-methyl violet) is 1:3 (PANI : MV), (c) poly(brilliant green-methyl violet) is 1:3 (BG : MV) and that of (d) poly(gentian violet-methyl violet) is 1:5 (GV : MV).

3.2. Electropolymerization of BG with GV, aniline with MV, GV with MV, BG with MV

The cyclic voltammograms of copolymerization of brilliant green and gentian violet (Fig. 5).

From Fig. 5, for the copolymerization of BG and GV the peak found at -550 mV is closer to that of the GV monomer than that of BG (the peaks of the copolymer and the GV are found roughly at about the same potential). Thus, the copolymer property is more related to the GV. But this cathodic peak of the copolymer is more intense by one and a half (1.5) times than the peak observed during the electropolymerization of the GV in the absence of BG. However, the anodic peak currents at around a peak potential of 1,500 mV and the high currents observed at far positive potential are almost equal for the electropolymerization of both gentian violet alone and gentian violet in the presence of brilliant green. This shows the presence of brilliant green enhances the rate of polymerization of gentian violet at the surface of glassy GCE. This shows BG has a catalytic effect on the electropolymerization of GV as it increases the rate of polymerization of GV.

During the electropolymerization of the aniline and MV, the change in current is similar to that of the voltammograms of electropolymerization of methyl violet. But, the cathodic peaks observed at about the same potential (-400 mV) are different in their intensity, i.e., the peak current of the copolymer (-3.80 mA) is greater than that of poly(MV) in the absence of aniline (-2.90 mA). This shows that the presence of aniline produces a high current.

For the copolymerization of the selected mole ratio of MV and GV, both the oxidation and reduction peaks were increased upon cycles and this is very visible in the first six cycles. The voltammogram has a shape similar to that of MV polymerization; therefore, the copolymer behaves as the poly(MV). The presence of GV has made a very small change in electropolymerization. Thus, the presence of GV enhances a little the rate of polymerization of MV at the surface of GCE. The cathodic peak current of the copolymer poly(GV-

MV) observed at about - 500 mV is about ten times when compared to that of the peak current of poly(GV) in the absence of MV. This shows MV has a catalytic effect on the electropolymerization of GV as it increases the rate of polymerization of GV.

On copolymerization of brilliant green and methyl violet, both the oxidation and reduction peaks were increased with cycles. The intensity of the oxidation and reduction peak currents of the copolymer is much greater than that of poly(brilliant green) which shows the catalytic effect of methyl violet.

3.3. Determination of Ascorbic Acid and Uric Acid by GC/Polydyes Modified Electrodes and Bare GC Electrode

The oxidation potentials of UA and AA are too close to be separately determined by using bare electrodes.

3.3.1. Determination of Ascorbic Acid and Uric Acid by Bare GC Electrode

The electrode was modified in that the 1:3 mole ratio of the two dyes (optimum mole ratio of the two dyes) was selected and scanned for fifteen cycles.

Figure 6 (A) shows the CV and (B) shows the DPV of the mixtures of ascorbic acid and different concentrations of uric acid on bare GCE. The two solution mixture voltammograms show only one irreversible potential peak in CV i.e., peaks: (a) and (b) at 566 mV and also one potential peak in DPV i.e., peaks: (a) and (b) at 380 mV on bare GCE.

3.3.2. Determination of AA and UA mixture with copolymer poly(brilliant green-gentian violet) modified GC Electrode

Figure 7 depicts the CV and DPV of a mixture of the solution AA and UA on GCE modified by the copolymer of BG and GV (poly(BG-GV)). The electrode was modified in the mixtures of the two dyes by a 1:3 mole ratio (optimum mole ratio of the two dyes) and scanned for fifteen cycles in the solution.

Figure 7 shows the existence of two separate potential peaks for the concentrations of AA and UA in both CV and DPV. The first potential peaks around 200 mV on CV and 100 mV on DPV are the peaks of UA and those at potentials 600 mV on CV and 450 mV on DPV are the peak potentials of AA. The peak currents of AA are equal and that of UA are not. This is because the concentration of AA is the same (2 mM) and the concentrations of UA are 2.5 mM and 5 mM for the smaller and higher peak currents, respectively.

Therefore, one can easily conclude from this that the modified GCE resolved the overlapped voltammetric responses of AA and UA to well-separated voltammetric peaks. The results showed that the electrocatalytic activity of the poly(BG-GV) copolymer-modified GCE were excellent when compared to bare GCE.

3.3.3. Determination of AA and UA mixture with copolymer poly(brilliant green-methyl violet) modified GC Electrode

Two separated peaks at around 300 mV and 600 mV on CV and 150 mV (for the small potential peaks) and 450 mV and 500 mV on DPV are observed in Fig. 8.

In both cases, the peaks at small potentials are the potential peaks of UA which were in different concentrations and those at high potentials are the potential peaks of AA. The peak current of the voltammogram (a) which is for 2.5 mM UA and 2 mM AA is lower than that of (b) (5 mM UA and 2 mM AA) on the peak of UA due to their concentration difference and that of AA is the same. From this, again the separation of potential peaks by Brilliant Green-Methyl Violet copolymer-modified GCE shows the ability of this copolymer film to enhance the electrode to separate the potential peaks of samples that show almost one peak on bare GCE.

3.4. Determination of the Area of the Modified Electrode

The determination of the area of the modified electrode was done with all polymers investigated, and their copolymers. The CV in bare GCE was scanned at different scan rates of 4 mM $K_3Fe(CN)_6$ in 1 M KNO_3 solution.

The square root of scan rate dependence of peak current was plotted and the Randles-Sevcik equation was applied to determine the Diffusion coefficient of $Fe(CN)_6^{3-}$ ion. This was used to determine the area after running the CV of 4 mM $K_3Fe(CN)_6$ in 1 M KNO_3 at different scan rates. From the plot of peak current vs. square root of scan rate shown in Fig. 9 (a), the slope was determined and this was used to determine the area from the Randles-Sevcik equation and the result is summarized in Table 1.

Table 1

Surface area of the different modified electrodes

Modified Electrode	Area/cm ²	Ip of DPV for 2 mM AA
Poly(BG-GV)	8.75 10 ⁻²	2.87 10 ⁻⁴
BG	1.20 10 ⁻¹	3.02 10 ⁻⁴
poly(ANI- MV)	1.27 10 ⁻¹	3.66 10 ⁻⁴
poly(BG-MV)	7.88 10 ⁻²	4.12 10 ⁻⁴
GV	1.10 10 ⁻¹	4.89 10 ⁻⁴
MV	1.44 10 ⁻¹	5.39 10 ⁻⁴
poly(GV-MV)	1.15 10 ⁻¹	7.12 10 ⁻⁴
PANI	7.86 10 ⁻¹	8.50 10 ⁻⁴
Bare GCE	7.10 10 ⁻²	5.40 10 ⁻⁵

The area of modified electrodes is decreased from PANI to poly(brilliant green-gentian violet) in the order of:

PANI > MV > MV-PANI > BG > GV-MV > GV > BG-GV > BG-MV

And in the decrement order of the peak current it can be put as:

PANI > GV-MV > MV > GV > BG-MV > MV-PANI > BG > BG-GV

After being modified with CV each one with fifteen cycles, the modified electrodes were scanned by DPV in 2 mM AA. From Table 1, the peak currents of the modified electrodes are greater than that of the peak currents of bare GCE raised from the increment of the areas of the electrodes.

The peak current is increased with the increase of the area of the modified electrodes and it is highest for the electrode with the largest area which is PANI with an area of 11 times and peak current 16 times greater than that of bare GCE and smaller for the smallest one, i.e., poly(BG-MV) copolymer with area 1.1 times greater than bare GCE and the peak current is $7^{1/2}$ times greater than that of bare GCE, respectively. This increment is because as the surface area of the electrode increases the microporous hole of the films produced over the modified electrode surface increases and this allows more and more electron transfer [19–21]. Though this case does for the two extremes and for some others, it is not consistent in all cases as can be seen, for instance, on BG and poly(BG-MV). In this case, the area of the electrode

modified by poly(BG) is about 1.7 times and the peak current is 5.6 times greater than that of bare GCE whereas the area of the electrode modified by poly(BG-MV) is 1.1 times and the peak current $7^{1/2}$ times greater than that of bare GCE. Even though the area of the first (1.7 times) is greater than the latter (1.1 times), the peak current of the electrode modified by poly(BG) is less than that of poly(BG-MV). This inconsistency is raised from another factor which is the kinetics of the nature of the film which slags the electron transfer to be increased by the area of the electrode. This inconsistency is also observed between poly(GV) and poly(MV-PANI), poly(MV) and poly(GV-MV) and some others due to the same reason [19–21].

Table 2
Electrochemical parameters of the studied modified electrodes (BG/GC, GV/GC, MV/GC, PANI/GC, BG-GV/GC, GV-MV/GC, BG-MV/GC, and PANI-MV/GC) at scan rate of 100 mV/s.

Modified Electrode	Epa/mV	Epc/mV	Ipa/mA	Ipc/mA	Ipa/Ipc	ΔE/mV
GV	348	204	0.058	-0.056	1.03	144
BG	203	67	0.05	-0.05	1	136
MV	396	215	0.33	-0.33	1	181
PANI	306	17	1.01	-0.78	1.3	289
Poly(BG-GV)	500	437	0.13	-0.12	1.08	63
Poly(BG-MV)	483	271	0.11	-0.07	1.57	212
poly(MV-GV)	438	233	0.23	-0.21	1.09	205
poly(ANI-MV)	464	216	0.33	-0.33	1	248

From Table 2, the ratio of anodic peak current to cathodic peak current (I_{pa}/I_{pc}) for poly(BG), poly(MV), and poly(ANI-MV) is equal to one. The (I_{pa}/I_{pc}) of the others are also close to one. This shows the electron transfer is high and therefore the processes are reversible.

4. Conclusion

The study successfully achieved the electrochemical polymerisation and characterization of gentian violet, brilliant green, aniline, and methyl violet, as well as their copolymers, on a GCE using an Ag/AgCl reference electrode. The modified electrode was then used to determine AA and UA, two electroactive species that usually show unresolved voltammograms on bare GCE. The copolymer/polymer electropolymerized modified electrode was able to separate the voltammetric peaks of both analytes, which originally showed overlapped voltammetric peaks on bare GCE.

The poly(brilliant green-gentian violet) film and poly(brilliant green-methyl violet) film, in particular, showed separated peaks of UA at 200 mV (the maximum separation) and 300 mV on CV, and at 100 mV and 150 mV on DPV, respectively. Meanwhile, the separated peaks of AA were observed at 600 mV on CV for both copolymers and at 450 mV and 500 mV on DPV for poly(brilliant green-gentian violet) film and

poly(brilliant green-methyl violet) film, respectively. The modification of the electrode by electrochemical polymerization of organic dye polymers resulted in an increased area of the working electrode from the range of $7.88 \times 10^{-2} \text{ cm}^2$ to $7.86 \times 10^{-1} \text{ cm}^2$. This also increased the peak currents, as the electron transfer increment by increasing the area of the electrode was observed. In conclusion, this study demonstrated that electrochemical polymerization of organic dye polymers can enhance the sensitivity of the electrode and develop simple, stable, and low-cost electrochemical sensors.

Declarations

Author Contribution

J. N. G., T. T. B., and S. T. A. Prepared the conception, S. T. A. secured the research fund, T. T. B. Organized the data, J. N. G has undergone the experimental work and wrote the draft manuscript, All authors reviewed the manuscript.

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References

1. K.M. Molapo, P.M. Ndangili, R.F. Ajayi, G. Mbambisa, S.M. Mailu, N. Njomo, M. Masikini, P. Baker and E.I. Iwuoha, *Electronics of Conjugated Polymers (I): Polyaniline*, Int. J. Electrochem. Sci., **2012**, 11859, 7.
2. J. Drzej dragan, Sylwia Sulimiera Michalak, *Gentian violet: what we know and what is ahead of us*, Article in Acta Poloniae Pharmaceutica, **2019**, 389, 76.
3. M.K. Mbacké, *Electrocoagulation process applied on pollutants treatment- experimental optimization and fundamental investigation of the crystal violet dye removal*, Journal of Environmental Chemical Engineering, **2016**, 402, 4.
4. Hayfaa A Mubarak, Laith Ali Abdul-Rahaim, Joseph Amoako-Attah, Rafid M Alkhaddar, *Electrochemical removal of brilliant green dye from wastewater*, Conf. Series: Materials Science and Engineering, **2020**, 012036, 888.
5. V.S. Mane and P.V. Babu, *Electrochemical removal of Brilliant green and Condo red dye from aqueous solutions*, Institute of Technology, Nirma University, Ahmedabad, **2011**, 2.
6. Z. Tong, *Adsorption Performance of Methyl Violet via Fe_2O_3 @Porous Hollow Carbonaceous Microspheres and Its Effective Regeneration through a Fenton-Like Reaction*, College of Environmental Science and Engineering, Chang'an University, Xi'an, China, **2016**, 13, 6.

7. Y. Su, *Electrophoretic deposition of graphene, carbon nanotubes and composite films using methyl violet dye as a dispersing agent*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, **2013**, 436, 97.
8. Zahraa A. Jarjes, Mohammed Razip Samian, Sulaiman Ab Ghani, *Conductive polymers: Their preparations and catalyses on NADH oxidation at carbon cloth electrodes*, Arabian Journal of Chemistry, **2015**, 727, 8.
9. Sibel Sezgin, Murat Ates, Elif A. Parlak, A. Sezai Sarac, *Scan Rate Effect of 1-(4-methoxyphenyl)-1H-Pyrrole Electro-coated on Carbon Fiber: Characterization via Cyclic Voltammetry, FTIR-ATR and Electrochemical Impedance Spectroscopy*. Int. J. Electrochem. Sci., **2012**, 1097, 7.
10. P. Rai, R. Gautam, S. Banerjee, V. Rawat and M. Chattopadhyaya, *Synthesis and characterization of a novel SnFe₂O₄@activated carbon magnetic nanocomposite and its effectiveness in the removal of crystal violet from aqueous solution*, Journal of Environmental Chemical Engineering, **2015**, 2281, 3.
11. Nitish Govindarajan, Aoni Xu, and Karen Chan, *How pH affects electrochemical processes*, Science, **2022**, 375, 380.
12. G. Liu, W. Ma, Y. Luo, D. Sun and S. Shao, *Simultaneous Determination of Uric Acid and Xanthine Using a Poly(Methylene Blue) and Electrochemically Reduced Graphene Oxide Composite Film Modified Electrode*, Journal of Analytical Methods in Chemistry, **2014**, 10, 1.
13. M. Ghica and C. Brett, *Poly(brilliant green) and poly(thionine) modified carbon nanotube coated carbon film electrodes for glucose and uric acid biosensors*, Talanta, **2014**, 9, 1.
14. V. Pifferi, M. Barsan, M. Ghica, L. Falciola and C. Brett, *Synthesis, characterization and influence of poly(brilliant green) on the performance of different electrode architectures based on nanotubes and poly(3,4-ethylenedioxythiophene)*, Electrochimica Acta, **2013**, 199, 98.
15. A. Baba, S. Tian, F. Stefani, C. Xia, Z. Wang, R. Advincula, D. Johannsmann and W. Knoll, *Electropolymerization and doping/dedoping properties of polyaniline thin films as studied by electrochemical-surface plasmon spectroscopy and by the quartz crystal microbalance*, Journal of Electroanalytical Chemistry, **2004**, 562, 95.
16. H. Xu, W. Zhang, W. Zhu, D. Wang, J. Ye, K. Yamamoto and L. Jin, *Simultaneous determination of total homocysteine, cysteine and methionine in hypothyroid patients' plasma by liquid chromatography using platinum/poly(methyl violet) modified electrode*, Analytica Chimica Acta, **2005**, 545, 182.
17. A. Cihaner, *Electrochemical Synthesis of Crowned Conducting Polymers: Nature of Radical Cations in Polymerization and Mechanism of Conductivity*, PhD Thesis, Middle East Technical University, **2004**, 3.
18. A. kujundziski, D. Chamovska and T. Grchev, *Electroconducting materials based on polypyrrole*, **2016**, 282, 57.
19. W. Wanga, Z. Weib, W. Sub, X. Fana, J. Liua, C. Yana and C. Zenga, *Kinetic investigation of vanadium (V)/(IV) redox couple on electrochemically oxidized graphite electrodes*, Electrochimica Acta, **2016**, 205, 102.

20. M. Hamza, R. Abdelhedi, E. Brillas and I. Sires, *Comparative electrochemical degradation of the triphenylmethane dye Methyl Violet with boron-doped diamond and Pt anodes*, Journal of Electroanalytical Chemistry, **2009**, 627, 41.
21. M.M. Barsan, E.M. Pinto and M.A. Brett, *Electrosynthesis and electrochemical characterisation of phenazine polymers for application in biosensors*, Electrochimica Acta, **2008**, 3973, 53.
22. G. Wei, W. Su, Z. Wei, X. Fan, J. Liu and C. Yan, *Electrocatalytic effect of the edge planes sites at graphite electrode on the vanadium redox couples*, Electrochimica Acta, **2016**, 263, 204.
23. A.A. Almeida, J.M. Dias, D.P. Santos, F.R. Nogueira, M. Navarro, J.N. Tonholo, D.P. Lima and A.S. Ribeiro, *A magenta polypyrrole derivatised with Methyl Red azo dye: synthesis and spectroelectrochemical characterization*, Electrochimica Acta, **2017**, 240, 239.

Supplementary Figures

Supplementary Figures S1 to S3 are not available with this version.

Figures

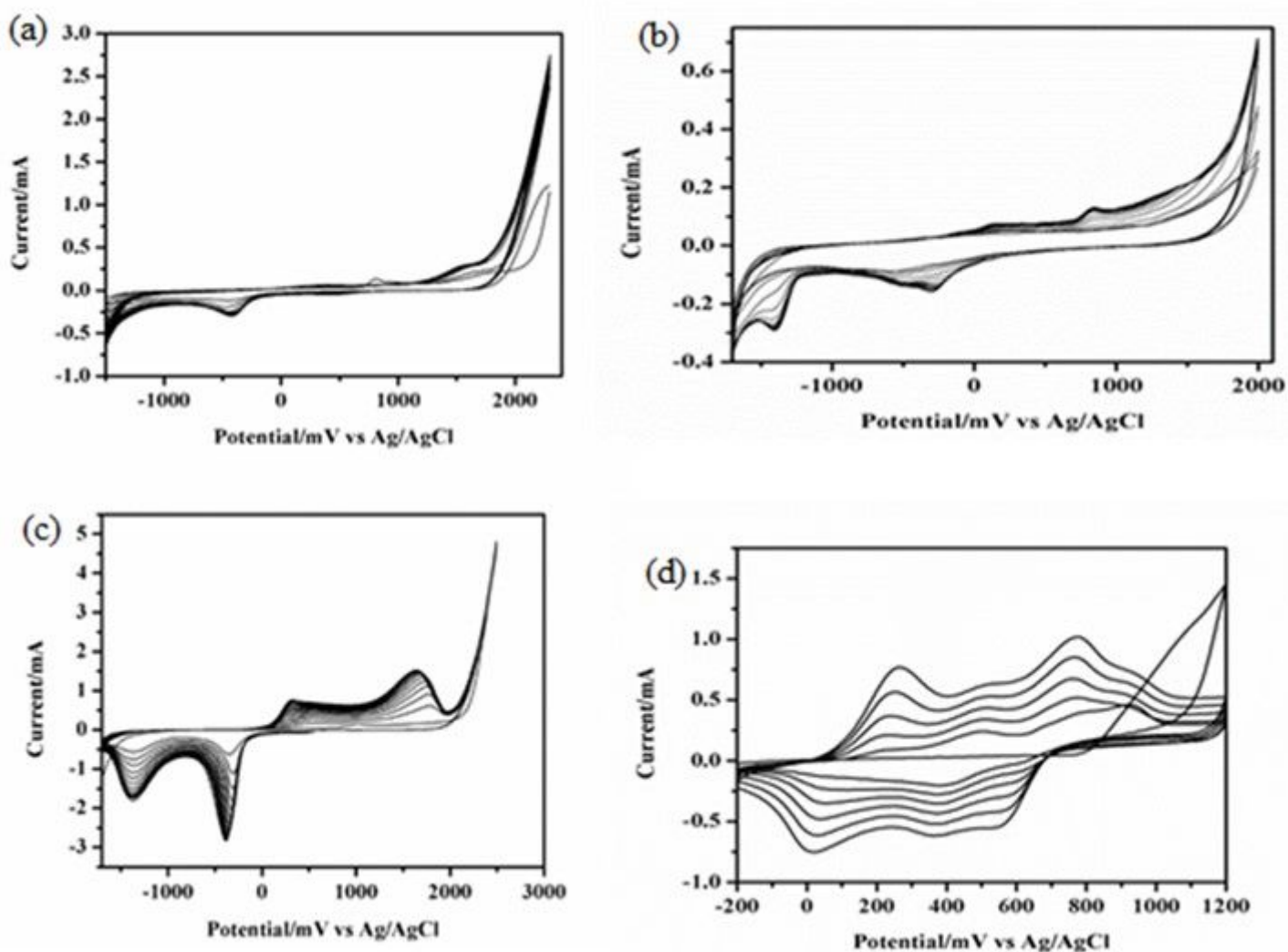


Figure 1

Voltammograms of electropolymerizations on GCE of (a) 2 mM Gentian Violet, 0.1 M phosphate buffer (pH 7.8) and 0.1 M Na_2SO_4 solution in the potential range from -1500 mV to 2500 mV, (b) a solution containing 10 mM BG aqueous solution, 0.5 M NaNO_3 and 0.025 M $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ buffer solution in the potential range from -1700 mV to 2100 mV, (c) MV from a solution containing 5 mM MV in 0.5 M H_2SO_4 solution in the potential range from -1700 mV to 3000 mV, (d) aniline during electrolysis of the solution consisting of 0.3 M H_2SO_4 and 0.4 M aniline. All electropolymerizations were done at a scan rate of 100 mV/s for a total of 15 cycles except for aniline which was done for a total of 6 cycles.

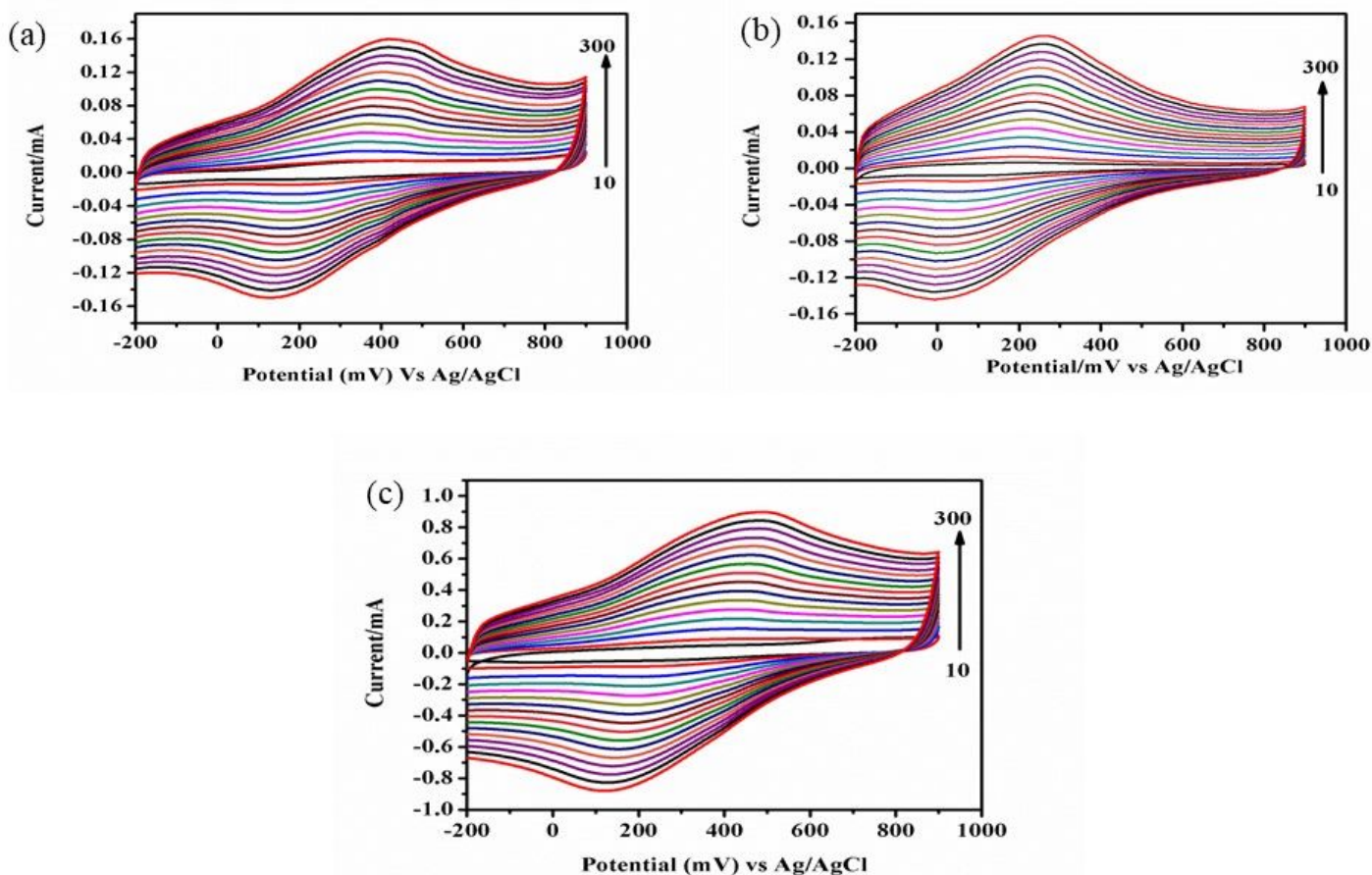


Figure 2

Cyclic voltammograms of: (a) poly(GV), (b) poly(BG), (c) poly(MV) film on GCE at scan rates of: 10, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, and 300 mV/s in 0.1 M H_2SO_4 solution.

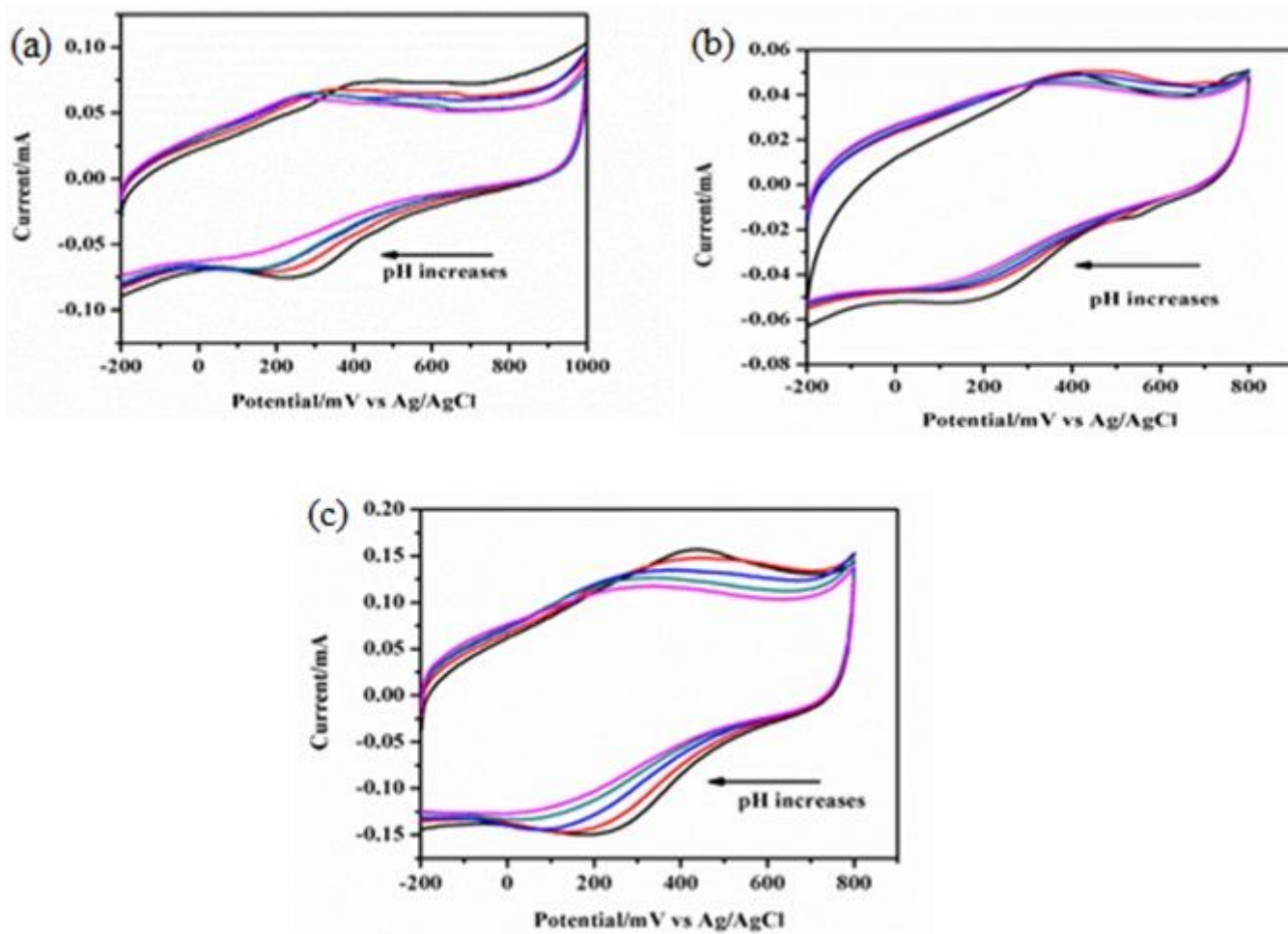


Figure 3

The pH dependence voltammogram of: (a) poly(GV), (b) poly(BG), (c) poly(MV) film coated GCE in the solution of 0.5 M Na_2SO_4 with different pHs at a scan rate of 100 mV/s. The pH values from right to left were 1.56, 2.32, 3.35, 4.07, and 5.30.

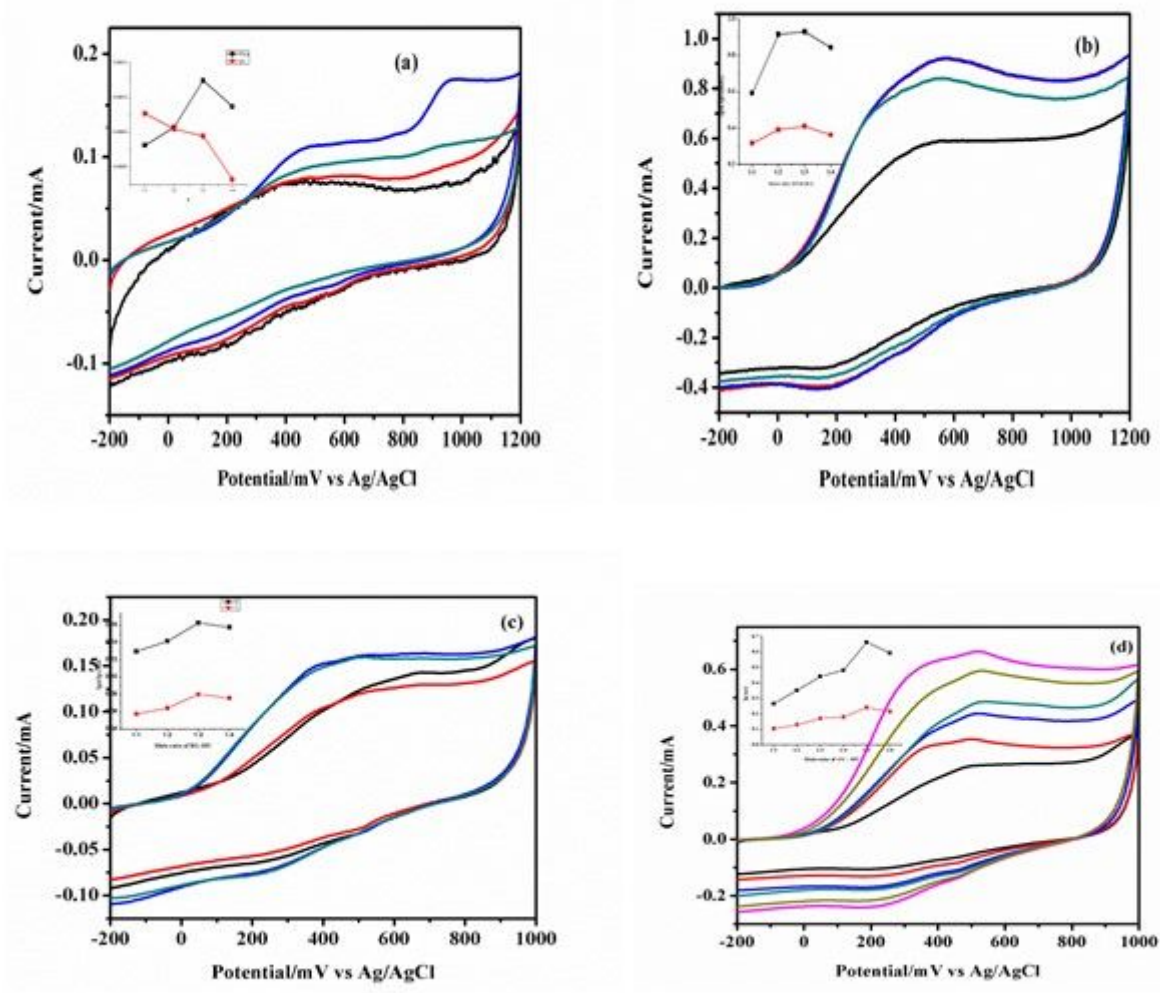


Figure 4

Optimization of copolymerization of the copolymer (a) poly(gentian violet-brilliant green), (b) poly(aniline-methyl violet), (c) poly(brilliant green-methyl violet), and (d) poly(gentian violet-methyl violet).

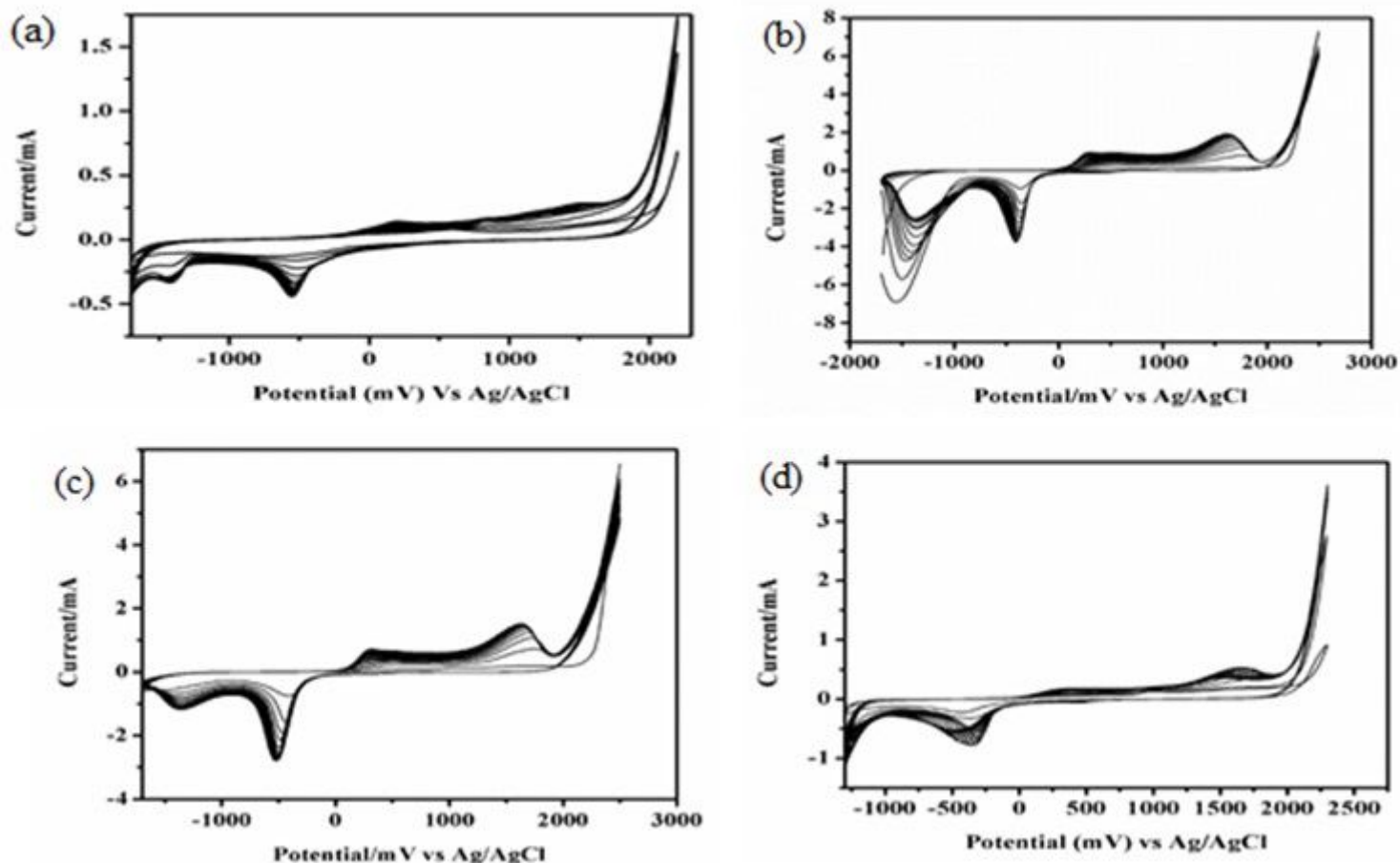


Figure 5

Voltammograms of copolymerization of: (a) BG and GV on GCE in the potential range from -1700 to 2200 mV; (b) aniline and MV during electrolysis of the solution consisting of 0.3 M H_2SO_4 , 5 mM methyl violet and 0.4 M aniline between the potential range from 1700 to 2500 mV, (c) the selected mole ratio of MV and GV; (d) BG and MV during electrolysis of the solution consisting of 10 mM BG aqueous solution containing 0.5 M $NaNO_3$ and 0.025 M K_2HPO_4 - KH_2PO_4 buffer solutions and solution consisting of 0.5 M H_2SO_4 , 5 mM MV between the potential range from -1700 to 2300 mV, all were done at a scan rate of 100 mV/s for 15 number of cycles.

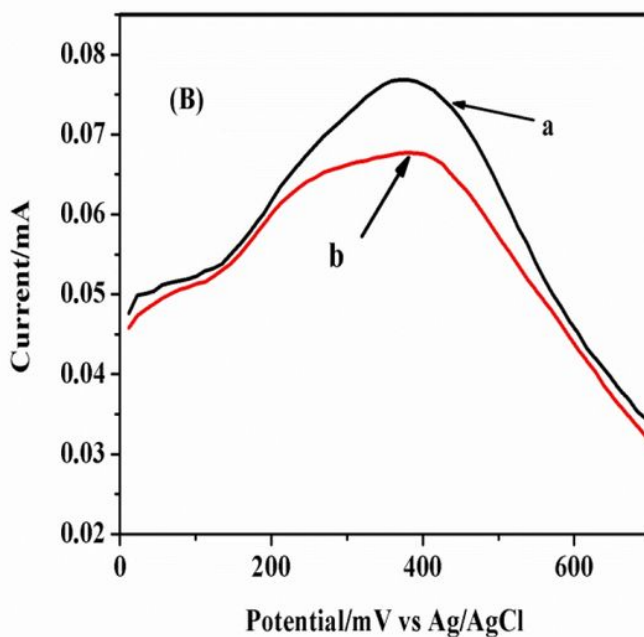
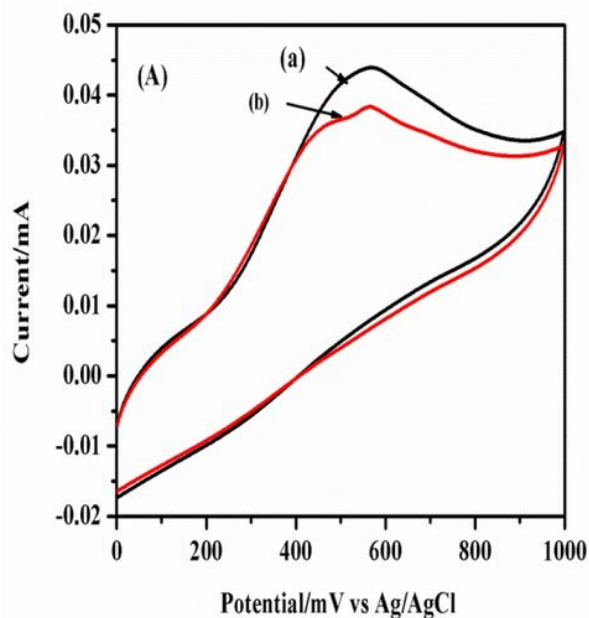


Figure 6

(A) The cyclic voltammogram and (B) differential pulse voltammogram of a mixture of 2 mM ascorbic acid and (a) 5 mM, (b) 2.5 mM, and (c) 1.25 mM uric acid solution on bare glassy carbon electrode at the scan rate of 100 mV/s.

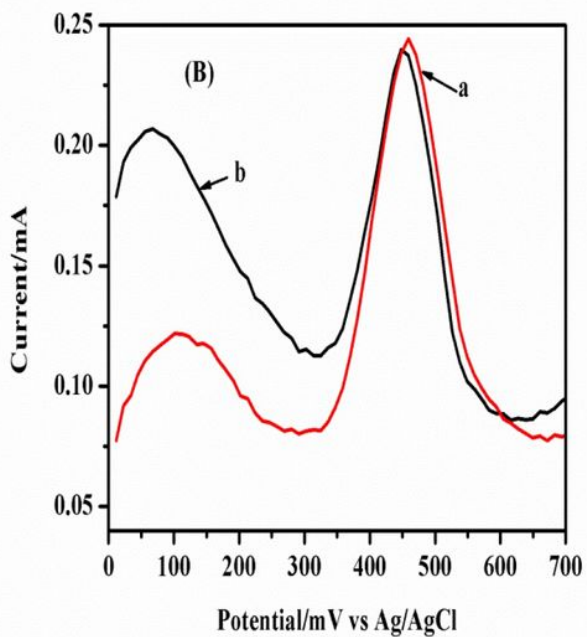
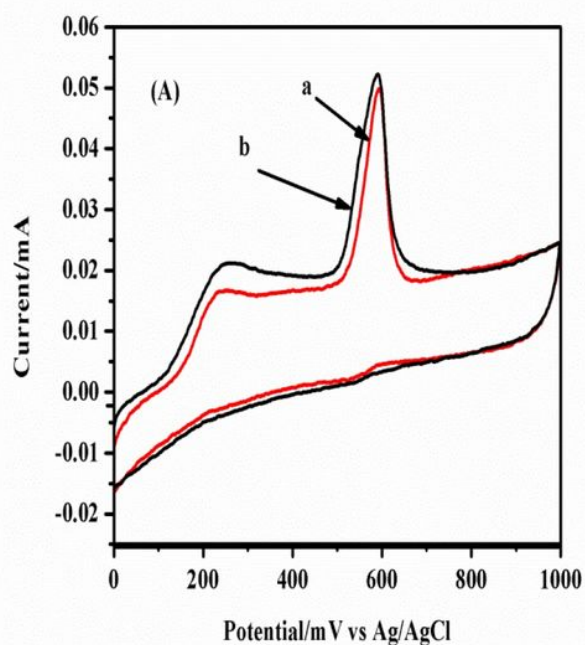


Figure 7

(A) The CV and (B) DPV of a mixture of 2 mM AA and, (a) 2.5 mM and (b) 5 mM UA solution on GC/poly(BG-GV) copolymer modified electrode at scan rate of 100 mV/s.

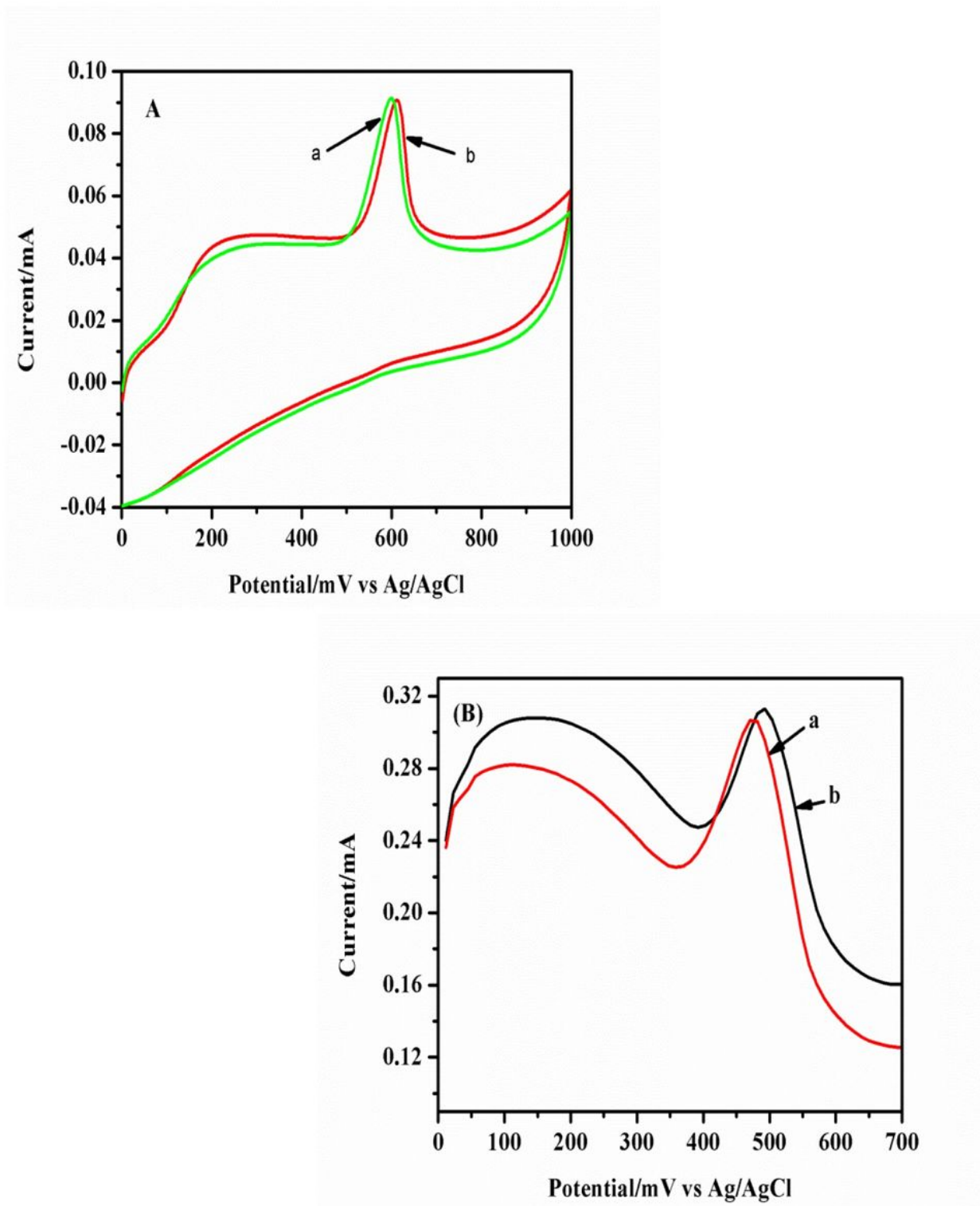


Figure 8

(A) The CV and (B) DPV of a mixture of 2 mM AA and (a) 2.5 mM and (b) 5 mM UA solution on GC/poly(brilliant green-gentian violet) copolymer modified electrode at a scan rate of 100 mV/s.

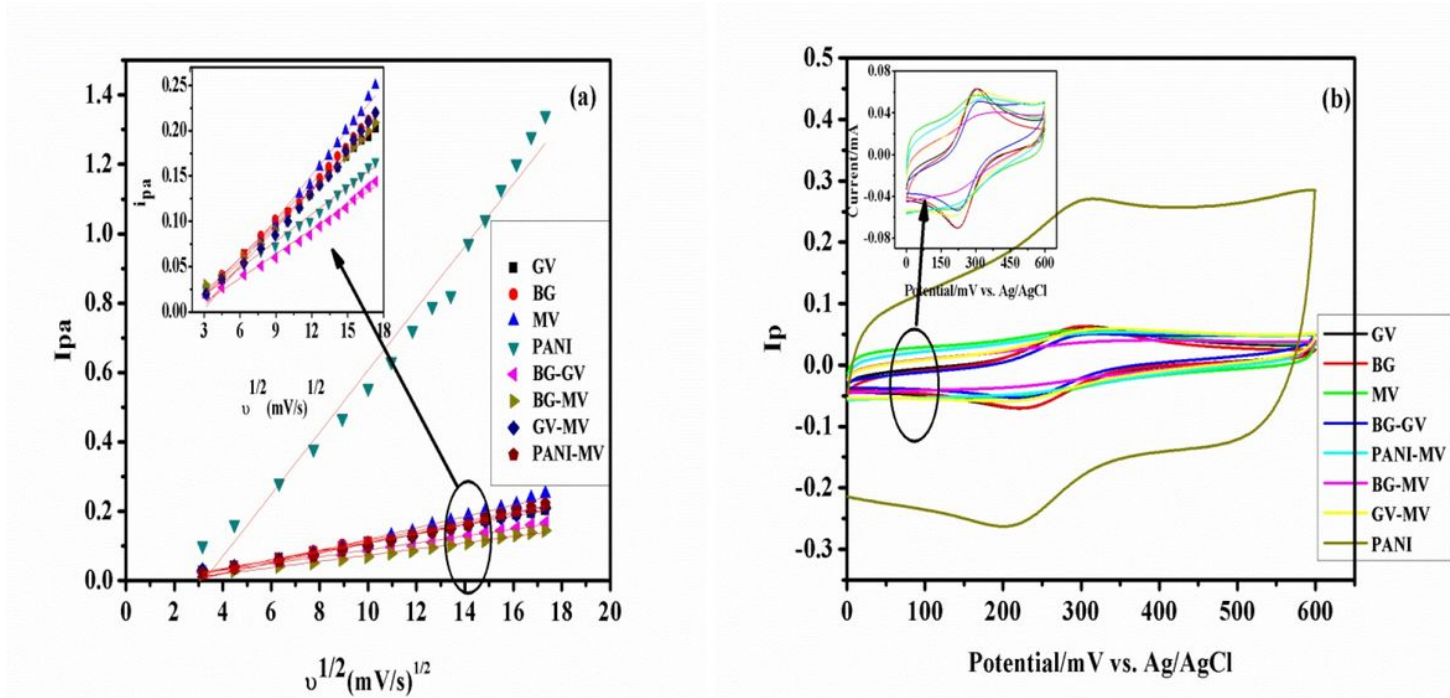


Figure 9

(a) The anodic peak current vs. square root of scan rates of BG/GC, GV/GC, MV/GC, PANI/GC, BG-GV/GC, GV-MV/GC, BG-MV/GC, and PANI-MV/GC evaluated from CV in 0.1 M H_2SO_4 (vs. Ag/AgCl reference) and (b) their corresponding voltammogram at scan rate of 100 mV/s.