COMPARATIVE STUDY OF SELF-ASSEMBLY AND ELECTROPOLYMERIZATION TECHNIQUES

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Abstract: Conducting polymer and self-assembled monolayer (SAM) of iron phthalocyanine complex are formed on glassy carbon electrode (GCE) and gold (Au) electrode, respectively. The polymer is formed via electropolymerization, while SAM is formed via self-assembly technique. Comparative studies of these techniques are carried out. Results of these studies show that the redox processes of the adsorbed species are closely related to those of the solution electrochemistry. Both ligand- and metal-based redox processes are observed on the MPc-polymer-modified surface, while only metal-based redox process is observed on the MPc-SAM-modified surface. Atomic force microscopic (AFM) images show differences in morphologies of the modified surfaces. Electrochemical impedance spectroscopic data suggest better electron transfer kinetics on the MPc-SAM-modified surface than that on the MPc-polymer-modified surface. The MPc-SAM-modified surface shows better electrocatalytic activity towards the oxidation of the herbicide, carbofuran, than the MPc-polymer-modified surface.

Keywords: Electropolymerization, self-assembly, iron phthalocyanine, impedance spectroscopy, carbofuran

Introduction

Self-assembly and electropolymerization techniques are two of the numerous methods of fabricating chemically modified electrodes (CMEs). A chemically modified electrode (CME) is an electrode having a chemical substance (organic or inorganic), deliberately immobilized on its surface, such that it exhibits the chemical, electrochemical, optical, and other important properties of the immobilized molecule(s) (Porter *et al.*, 1987). Chemical modification offers the possibility of intelligently reconstructing the surface of conventional electrodes, to enhance their functionality, by making use of the intrinsic properties of the modifier for selective electrochemical reactions. Chemical modification increases heterogeneous electron transfer rates of solution species, for which electron transfer process is thermodynamically possible, but kinetically limited. Kinetic limitation is attributed to high over potentials associated with redox processes involving such species on bare electrodes. Surface modification does not necessarily incorporate the electronic orbital system of the surface-immobilized species into the conduction band of the electrodes, but electron transfer rates are customarily fast for these species, because of their close proximity to the electronically conducting electrodes. This enhances their ability to mediate, via surface-confined redox couples, in electron transfer processes involving the electrodes and the analytes. Efficient mediatory role encompasses: (i) electrochemical reversibility, (ii) fast electron transfer between mediator, electrode and analyte, and (iii) chemical stability in the reaction environment.

Usually, chemical modifiers of interest in electroanalysis are: organic redox compounds, organometallic redox complexes, conducting polymers and fine metallic particles.

In this work, gold and glassy carbon electrodes are chemically modified with redox active Metalophthalocyanine (MPc) complex (Fig. 1). Gold electrode is modified via self-assembly technique, while glassy carbon electrode is modified via electrochemical polymerization. Fabrication of CMEs via self-assembly occurs by adsorption of molecules, from a homogeneous solution, onto a suitable substrate. Thio-substituted MPc complexes are normally employed for the modification of gold electrode via self-assembly, due to the affinity of sulphur for gold (Ozoemena *et al.*, 2001; Agboola *et al.*, 2007). The gold electrode is immersed in homogeneous solution of the MPc complex. The modified electrode is designated MPc-self-assembled monolayer (SAM)-modified electrode.

Electrochemical polymerization is facilitated by the presence of oxidizable groups (sulphur and nitrogen atoms) on the chemical modifier of interest (Goux *et al.*, 2003). The process is carried out by repetitive cycling, within suitable potential window, of a conductive substrate in a homogeneous solution of the monomer. Differences between successive voltammetry scans and emergence of new voltammetric peaks are characteristic of polymer formation (Obirai *et al.*, 2003). The elegance of this method is underscored by its simplicity and the ability to control polymer growth, with a fixed number of voltammetry cycles. Importantly, the quality of an MPc-based polymer is dependent on the nature of solvent, purity of the monomer and potential range employed during voltammetry scanning.

In this work, self-assembled monolayer of octa-substituted alkylthio-derivatised MPc complex (Fig. 1) (Akinbulu and Nyokong, 2009) is formed on polycrystalline gold disc electrode, while it's conducting polymer is formed on glassy carbon electrode. This MPc complex (Fig. 1) has the dual attribute of being suitable for forming both self-assembled monolayer and conducting polymer, on electronically conducting electrode, thus its relevance in this work.

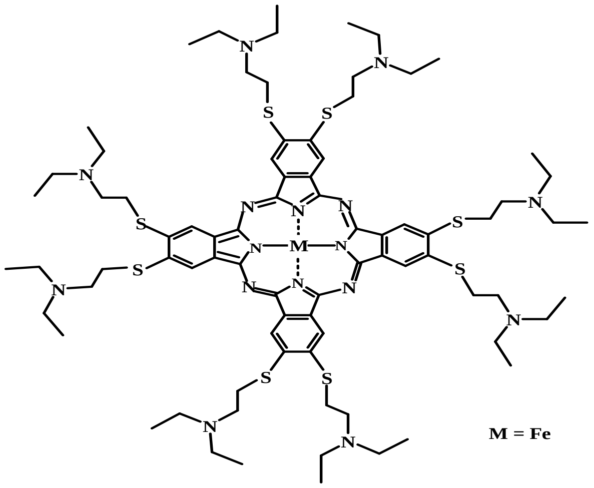


Fig. 1: Molecular structure of octa-substituted FePc complex

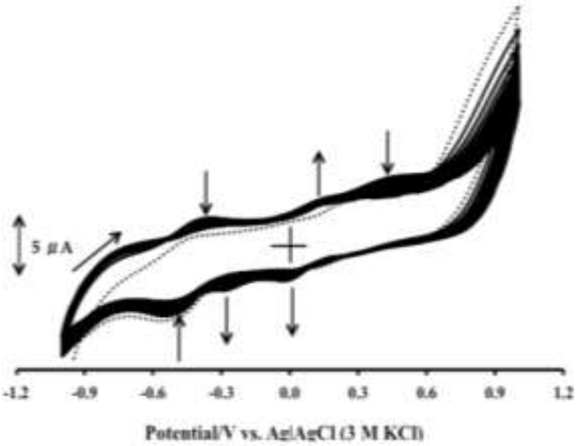


Fig. 2: Evolution of cyclic voltammetry profiles during repetitive scanning (20 cycles) of bare GCE in 1 × 10^{-3} M solution of MPc complex in freshly distilled DMF containing 0.1 M TBABF$_4$. Scan rate: 100 mV/s. Dotted line = First scan

The focus of the current work is to carry out comparative studies of these two techniques, in other to identify the effects of modification technique on morphology, electrical conductivity and electrocatalytic property of the resulting modified surfaces. It is expected that these properties will be significantly affected by the technique employed for modification, hence the relevance of the current work. Morphological studies were probed using atomic force microscopy and cyclicvoltammetry. Electrical conductivity of the modified electrodes was examined using impedance spectroscopy, while their electrocatalytic relevance was interrogated in the electroanalysis of the insecticide, Carbofuran (Fig. 2).

Materials and Methods

Materials

Dimethylformamide (DMF), sulphuric acid, hydrogen peroxide, acetic acid and sodium hydroxide were obtained from Merck. Carbofuran, tetrabutylammoniumtetrafluoroborate (TBABF$_4$) (electrolyte for electrochemical experiments involving MPc complexes) and phosphate buffer tablets were obtained from Sigma-Aldrich. Potassium chloride and potassium ferrocyanide were obtained from SAARCHEM. All solvents were distilled before use. Stock solution of carbofuran was prepared in freshly distilled methanol due to its limited solubility in water. Prior to electrochemical analysis, carbofuran was hydrolyzed in 0.5 M NaOH solution for 0.5 h, and the pH of the resulting solution adjusted to 4 with acetic acid.

Electrode modification

Prior to use, the electrode (GCE) surface was polished with alumina on a Buehler felt pad and rinsed with excess Millipore water. The gold electrode surface was also polished in aqueous slurry of alumina on sic-emery paper and subjected to ultrasonic vibration in absolute ethanol to remove residual alumina. The electrode was then etched in hot 'piranha' solution (30% H$_2$O$_2$ and concentrated H$_2$SO$_4$) (1:3 v/v) for two minutes and rinsed with excess Millipore water. It was then scanned in 0.5 M H$_2$SO$_4$ between -0.5 to 1.5 V vs. Ag|AgCl(3 M KCl) to obtain a reproducible scan.

The pre-treated polycrystalline gold disc electrode was rinsed with freshly distilled DMF and then immersed in a homogenous solution of the MPc complex (1 × 10^{-3} M) in DMF for 24 h.

Conducting polymer of MPc complex was formed on GCE by repetitive cyclic voltammetry scanning of the bare electrode in 1 x 10^{-3} M of theMPc complex in freshly distilled DMF containing 0.1 M TBABF$_4$ supporting electrolyte.

Electrochemical methods

Electrochemical experiments were performed using Autolabpotentiost at PGSTAT 302 (Eco Chemie, Utrecht, The Netherlands) driven by the general purpose Electrochemical System data processing software (GPES, software version 4.9). For all electrochemical experiments, a conventional three-electrode system was used. The working electrode was bare or MPc-modified glassy carbon electrode (GCE, with geometric area of 0.07 cm^2) or MPc-SAM-modified polycrystalline gold disc electrode (Au, with geometric area of 0.02 cm^2). Ag|AgCl(3 M KCl) or Ag|AgCl and platinum wire were used as reference and auxiliary (counter) electrodes, respectively. Electrochemical experiments involving MPc complex were performed in freshly distilled DMF, containing TBABF$_4$ as supporting electrolyte. All electrochemical experiments were carried out in argon saturated solutions. Electrochemical impedance spectroscopy (EIS) measurements were performed with Autolab FRA software between 1.0 MHz and 10 KHz using a 5 mV rms sinusoidal modulation. A non-linear least squares (NNLS) method based on the EQUIVCRT programme (Boukamp, 1986**)** was used for automatic fitting of EIS data.

Microscopic method

Morphological properties of modified electrodes were investigated using atomic force microscope (AFM). AFM images were obtained in the non-contact mode in air with a CP-11 Scanning Probe Microscope from Veeco Instruments (Carl Zeiss, South Africa) at a scan rate of 1 Hz. For atomic force microscopic studies, MPc-SAM was formed on gold-coated glass, while poly-MPc was formed on indium tin oxide (ITO) glass. The process of SAM formation on gold-coated glass was as reported for SAM formation on gold disc electrode, while poly-MPc was formed on ITO glass as reported for the formation of poly-MPc on GCE.

Results and Discussions

Modification of electrodes

Electropolymerization

Figure 2 shows the evolution of cyclic voltammetry profiles obtained during repetitive cyclic voltammetry scanning (twenty cycles) of bare GCE in 10^{-3} M of MPc complex in freshly distilled, dried DMF, containing 0.1 M TBABF$_4$. The best voltammetry response of the analyte (Carbofuran) on the MPc-modified GCE was obtained with the MPc-polymer formed from twenty voltammetry cycles. Hence the use of this number of voltammetry scans for electropolymerization. The thickness and electrocatalytic importance of electropolymerized film of MPc complex are dependent on the number of voltammetry cycle during electropolymerization (Akinbulu and Nyokong, 2009). The dotted line in Fig. 2 is the first cyclic voltammetry scan. Emergence of new cathodic peaks [E_p = -0.29 and -0.04 V versus Ag|AgCl (3 M KCl)] and anodic peak [E_p = +0.14 V versus Ag|AgCl] indicates changing nature of the electrode surface and film formation via electropolymerization. Electropolymerization of MPc complexes is aided by the formation of radicals from substituent containing oxidizable groups, such as sulphur and nitrogen (Goux *et al.*, 2003). In the present work, oxidation involving the tertiary amine group of the diethylaminoethanethio substituent may have facilitated electropolymerization. After modification, the electrode was rinsed in DMF, dried in a slow stream of argon and characterized. The modified electrode is designated poly-MPc-GCE.

Self-assembly

MPc-SAM-modified gold electrode was designed by immersing the bare gold disc electrode in DMF solution of the

MPccomplex, for 24 h. Formation of SAM may have been promoted by coordination of the sulfur group (using its lone pairs of electrons) to gold, with the C-S bond intact after SAM formation, as reported previously (Ozoemena *et al*, 2003).

Cyclic voltammetry responses of modified electrodes

Figure 3 shows the cyclic voltammetry profiles of bare GCE (dashed lines) and poly-MPc-GCE (bold line) in pH 4 buffer solution. The best current response of the herbicide, carbofuran, discussed later, was obtained at this pH value, hence its use for voltammetry characterization of the modified electrode. No redox process was observed on bare GCE. The cathodic peak labeled **I** [*E*p = -0.22 V vs. Ag|AgCl (3 M KCl)], and anodic peak labeled **II** [*E*p = +0.72 V vs. Ag|AgCl(3 M KCl)] confirms the presence of the polymeric film of the MPccomplex on the modified-GCE. Processes **I** and **II** are assigned to $Fe^{II}Pc^{-2}/Fe^{I}Pc^{-2}$ and $Fe^{III}Pc^{-1}/Fe^{III}Pc^{-2}$ couples, respectively. These redox processes were also observed in the solution electrochemistry of thisMPc complex (Akinbulu and Nyokong, 2009). Process **I** is less-resolved than process **II.** The ill-resolved nature of metal-based process has been reported for SAM of iron phthalocyanine complex (Ozoemena and Nyokong, 2002). Therefore, it is not surprising that this behavior was observed for the electroplymerized film of the complex.

Figure 4 shows the cyclic voltammetry response of MPc-SAM modified gold electrode in pH 4 buffer solution. Apart from the fact that the best voltammetry response of the herbicide, carbofuran, was obtained at this pH, the MPc-SAM-modified gold electrode was appreciably stable at this pH. Only metal-based redox process of the adsorbed MPc complex was observed (Fig. 4). The half-wave potential of the redox process, +0.22 V versus Ag|AgCl (3 M KCl), suggests the process can be associated with Fe^{III}/Fe^{II} redox couple (Ozoemena & Nyokong, 2002). This process is better resolved than the metal-based process observed on poly-MPc-GCE.

Although, the electrodes modified were different (glassy carbon and gold), with different potential window employed in Figs. 3 and 4, it is instructive to observe that electropolymerized film of the MPc complex is more electrochemically sensitivity than the MPc-SAM film. This submission is hinged on the fact that both metal ($Fe^{II}Pc^{-2}/Fe^{I}Pc^{-2}$) and ligand-based ($Fe^{III}Pc^{-1}/Fe^{III}Pc^{-2}$) processes were observed on poly-MPc-modified GCE (Fig. 3). This may be attributed to the fact that electrochemical polymerization allows for the formation of multilayer film of MPc complex, while only a monolayer film of the complex can be formed via self-assembly method (Nyokong and Bedioui, 2006).

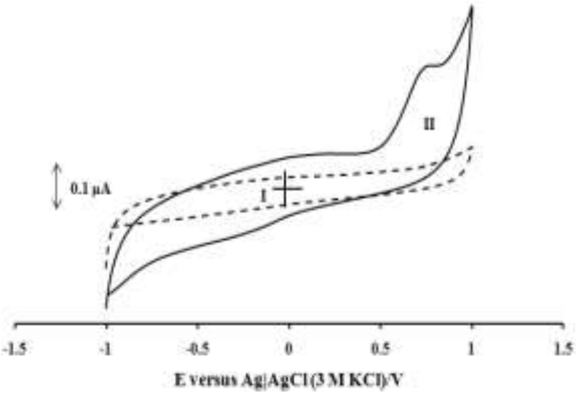


Fig. 3: Cyclic voltammetry profile of bare GCE (dashed lines) and poly-MPc-GCE (bold line) in pH 4 buffer solution. Scan rate: 100 mV/s

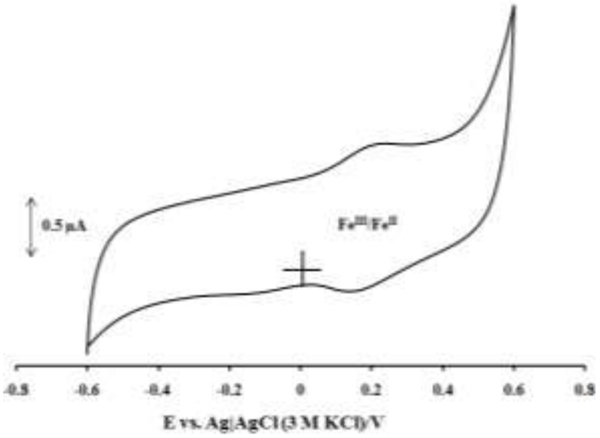


Fig. 4: Cyclic voltammetry profile of MPc-SAM-Au in pH 4 buffer. Scan rate: 100 mV/s

Scanning electron microscopic responses of modified electrodes

Figures 5 (A-D) shows the AFM images of bare gold-coated glass, bare ITO glass, MPc-SAM-modified gold-coated glass and poly-MPc-modified ITO glass, respectively. There are distinct differences in morphologies of these surfaces. The bare surfaces are significantly rough, unlike the modified surfaces. The MPc-SAM-modified gold-coated surface is porous in nature, unlike the much more compact poly-MPc-modified ITO glass. The porous nature of the SAM-modified surface may be associated with some defects in the SAM. This is not unexpected, considering the molecular architecture of the MPc complex (Fig. 1), the precursor for the SAM in this work, unlike alkanethiols, which are remarkable for forming compact, densely packed and substantially defect-free SAMs (Porter *et al.*, 1987). The high possibility of forming a multilayer, via electropolymerization technique, may have contributed significantly to the compact nature of the poly-MPc-modified surface.

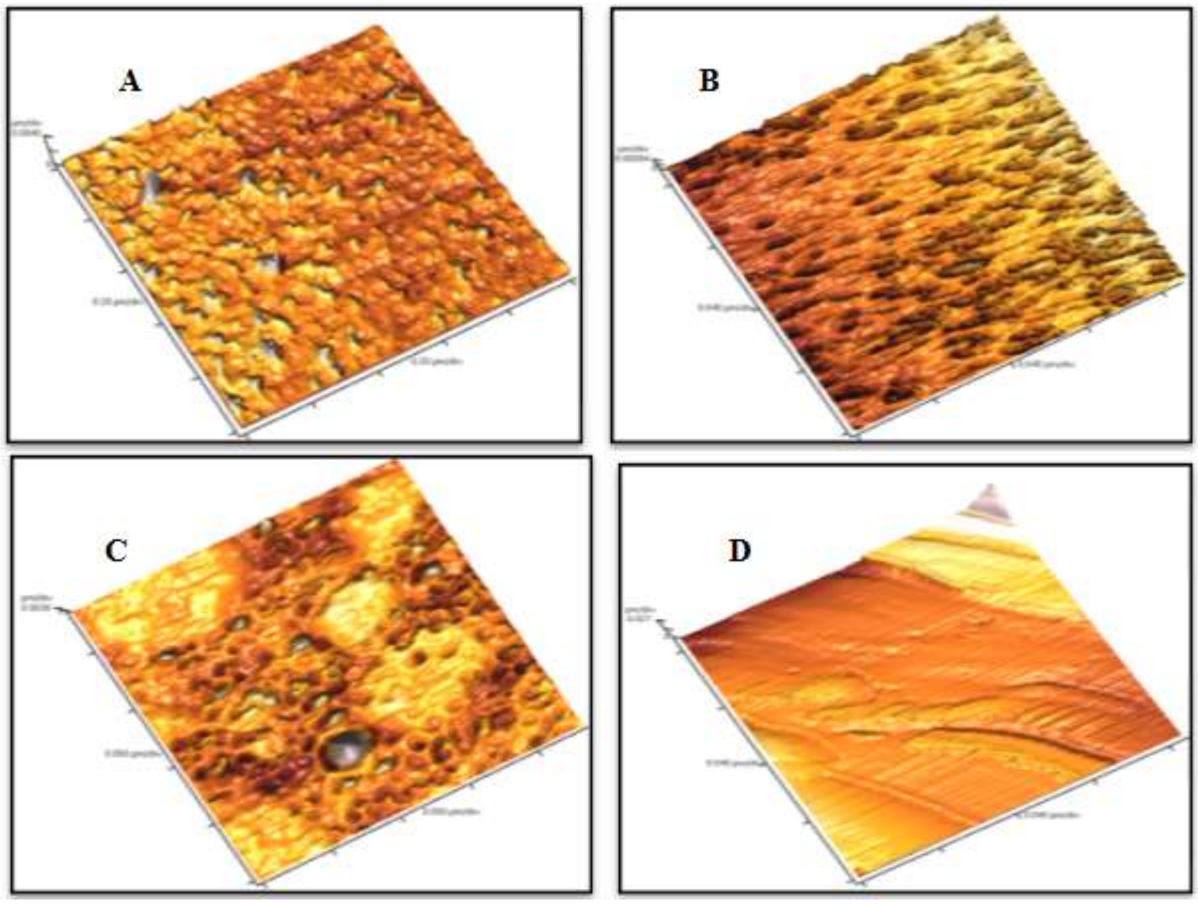


Fig. 5: AFM images of bare gold-coated glass (A), bare ITO glass (B), MPc-SAM modified gold-coated glass (C) and poly-MPc-ITO (D)

Impedimentary responses of modified electrodes

Nyquist plots

Figure 6 shows the fitted impedance data (Nyquist plots) of MPc-SAM-modified gold electrode and poly-MPc-modified glassy carbon electrode in 1 × 10^{-3} M solution of $K_3[Fe(CN)_6]$, containing 0.1 M KCl, as supporting electrolyte. The impedance spectra of the modified electrodes show a semi-circle, characteristic of charge transfer-limited impedance, in the high- frequency region, and a straight line, associated with a purely diffusion-limited reaction, in the low-frequency limit. Inset in Fig. 6 is the suitable equivalent circuit representative of this behavior. Where R_S is the resistance of the electrolyte solution between the reference and the working electrodes, R_{CT} is the charge transfer resistance, Z_W is mass-transfer or Warburg impedance and C_{dl} is the double-layer capacitance, which mimics the capacitance of the electrochemical double layer of the cell.

Values of R_{CT} show that resistance to charge transfer is higher on poly-MPc-modified glassy carbon electrode (6.10 KΩ ± 0.15) than on MPc-SAM-modified gold electrode (5.92 KΩ ± 0.12). These values are consistent with the diameters of the semicircular regions of the impedance spectra shown in Fig. 6. This shows that electron transfer process is better on the MPc-SAM film than on the electropolymerized film.

Usually, electron transfer between electrode andanalyteoccurs through quantum mechanical tunneling, over a particular distance. The multilayer nature of the electropolymerized film suggests higher tunneling distance between poly-MPc-GCE and the analyte than that between the monolayer MPc-SAM-modified gold electrode and the analyte. The shorter tunneling distance associated with the MPc-SAM-modified gold electrode may have resulted in R_{CT} of 180 Ω less than that of poly-MPc-modified glassy carbon electrode.

C_{dl} for poly-MPc-modified glassy carbon electrode (0.58 μF ± 0.05) and MPc-SAM-modified gold electrode (0.18 μF ± 0.02) suggests that the poly-MPc-GCE surface exhibits better capacitive behavior than the MPc-SAM-Au surface. This implies that the poly-MPc-modified surface may be a better material than the MPc-SAM-modified surface for designing charge storage devices.

Warburg impedance, Z_W, is a measure of the rate of diffusion of electroactive species within the modified surfaces. MPc-SAM-modified surface has higher value of Z_W (4.9 ± 0.12) × 10^{-5} $\Omega\ s^{-1/2}$) than poly-MPc-modified surface (4.3 ± 0.14) × 10^{-5} $\Omega\ s^{-1/2}$). This implies that electroactive species diffuse faster within the MPc-SAM-modified surface than within the poly-MPc-modified surface. This result is consistent with the morphological differences revealed by the AFM images in Fig. 5, corroborating our submissions thereof.

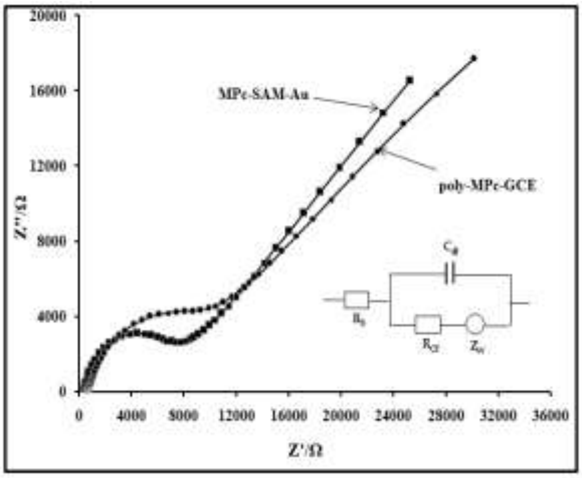


Fig. 6: Impedance spectra obtained forMPc-SAM-Au and poly-MPc-GCE in 1 × 10^{-3} M solution of $K_3[Fe(CN)_6]$ containing 0.1 M KCl as supporting electrolyte. Applied potential = 0.10 V versus Ag|AgCl (3 M KCl). Inset: Suggested circuit diagram

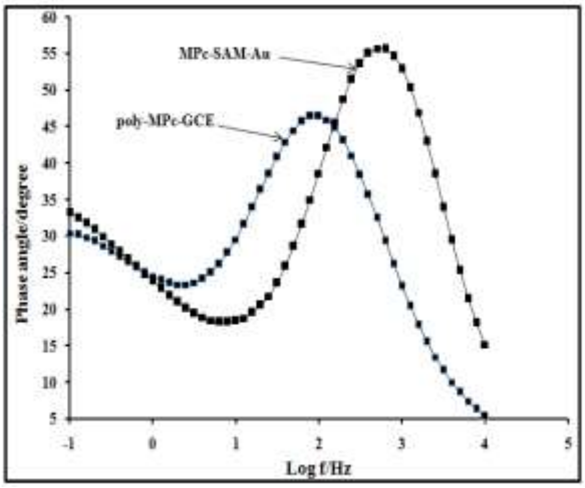


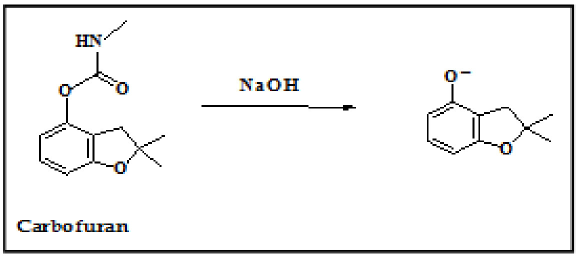
Fig. 7: Bode plots obtained for MPc-SAM-Au and poly-MPc-GCE in 1 × 10^{-3} M solution of $K_3[Fe(CN)_6]$ containing 0.1 M KCl as supporting electrolyte. Applied potential = 0.10 V versus Ag|AgCl (3 M KCl)

Bode plots

The frequency and the corresponding phase angle, for each of the modified surfaces, were estimated from the Bode plots in Fig. 7. For the MPc-SAM-modified gold electrode, the values are 500 Hz and 56° for frequency and phase angle, respectively. For the poly-MPc-modified glassy carbon electrode, the frequency and phase angle are 100 Hz are 46°, respectively. The phase peak in a Bode plot is derived from a serial combination of R_S with a parallel combination of R_{CT} and C_{dl}. As R_{CT} decreases, phase peak shifts to higher value and vice versa. These results are consistent with this submission. MPc-SAM-modified gold electrode with smaller value of R_{CT}(5.92 KΩ ± 0.12) has higher phase peak, while poly-MPc-modified GCE with larger value of R_{CT}(6.10 KΩ ± 0.15) has lower phase peak.

Electrocatalytic oxidation of carbofuran on modified electrodes

Electrocatalytic oxidation of the insecticide, carbofuran, was carried out on the modified electrodes. Carbofuran is not electroactive, hence the need for hydrolysis prior toelectrocatalysis. The electroactive phenolic analogue was generated via hydrolysis (Scheme 1).



Scheme 1: Alkaline hydrolysis of carbofuran

Figure 8 shows the cyclic voltammetry responses of the modified electrodes in 100 µM solution of carbofuran. These responses appear at lower potential, on each of the modified electrodes, compared to the responses on the respective bare electrodes (not shown), which suggests electrocatalysis. The current response, 1.14 µA, at a potential of +0.40 V versus Ag|AgCl (3 M KCl), observed on the MPc-SAM-modified gold electrode, is better than that observed on poly-MPc-GCE (0.72 µA, at a potential of 0.68 Vversus Ag|AgCl (3 M KCl). This indicates that, apart from better current response, electrocatalytic oxidation of carbofuran was more electrochemically feasible on the MPc-SAM-modified gold electrode than on poly-MPc-GCE. The current responses are consistent with the values of R_{CT} for the respective modified electrodes, supporting our submission thereof.

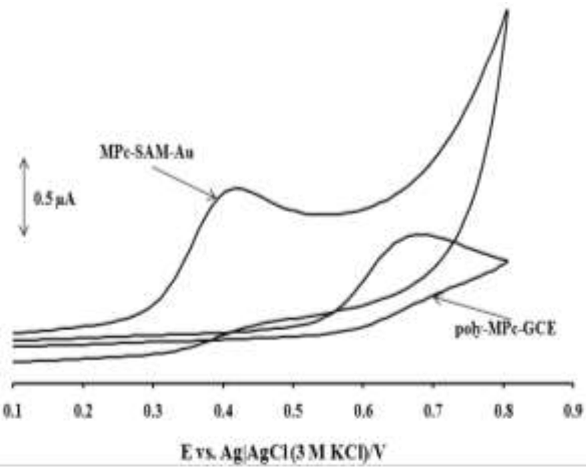


Fig. 8: Cyclic voltammetry profiles of poly-MPc-GCE and MPc-SAM-Au in 100 µM solution of carbofuran (pH 4). Scan rate: 100 mV/s

Mechanism of electrocatalytic oxidation of carbofuran

The potentials at which oxidation of carbofuran occurred on the modified electrodes suggest that different surface-confined redox couples may be involved in mediation of the process, in each case. Oxidation potential of carbofuran on the MPc-SAM-modified gold electrode suggests the involvement of Fe^{III}/Fe^{II} redox couple in electrocatalysis. On the other hand, oxidation potential of this insecticide on poly-MPc-GCE shows the involvement of $Fe^{III}Pc^{-1}/Fe^{III}Pc^{-2}$ redox couple in electrocatalysis. The suggested mechanisms are as follows:

Mechanism of electrocatalytic oxidation on poly-MPc-GCE

$Fe^{III}Pc^{-2} \longrightarrow Fe^{III}Pc^{-1} + \mathbf{e^-}$ (i)

$Fe^{III}Pc^{-1} + \mathbf{RO^-} \longrightarrow Fe^{III}Pc^{-2} + \mathbf{RO^\cdot}$ (ii)

Mechanism of electrocatalytic oxidation on MPc-SAM-Au

$Fe^{II}Pc^{-2} \longrightarrow Fe^{III}Pc^{-2} + \mathbf{e^-}$ (iii)

$Fe^{III}Pc^{-2} + \mathbf{RO^-} \longrightarrow Fe^{II}Pc^{-2} + \mathbf{RO^\cdot}$ (iv)

The phenolic species of carbofuran (Scheme 1) is represented as $\mathbf{RO^-}$ in the above mechanisms Regeneration of $Fe^{III}Pc^{-2}$ and $Fe^{II}Pc^{-2}$ redox species in step (ii) and (iv), respectively, indicates electrocatalysis

Conclusion

Comparative study of self-assembly and electropolymerization techniques were carried out. The modified electrode designed via electropolymerization was found to be electrochemically more sensitive than the modified electrode designed via self-assembly. This was attributed to the multilayer nature of the electropolymerized film, in comparison to the monolayer nature of the film formed via self-assembly. AFM images of the modified surfaces show striking morphological differences. The monolayer MPc-SAM-modified surface shows some defects, in contrast to the much more compact poly-MPc-modified surface. Impedance spectroscopic data show that the MPc-SAM film has lower charge transfer resistance, R_{CT}, lower capacitance, C_{dl}, but higher Warburg impedance, Z_W, than the poly-MPc film. Higher R_{CT}, associated with poly-MPc-GCE, suggests poorer electron transfer process. This was justified by higher tunneling distance, characteristic of the multilayered poly-MPc-modified surface. Better electron transfer process on the MPc-SAM-modified surface resulted in better electrocatalytic activity towards the oxidation of carbofuran. The oxidation potentials of carbofuran on the modified electrodes denote the involvement of Fe^{III}/Fe^{II} and $Fe^{III}Pc^{-1}/Fe^{III}Pc^{-2}$ redox species in electrocatalysis on MPc-SAM-modified gold and poly-MPc-modified glassy carbon electrode, respectively.

Conflict of Interest

Authors declare that there is no conflict of interest.

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