



## Theoretical Study of The Structure and Tautomerism of An Asymmetric Diimine Schiff Base, Preparation and Characterization of Its Modified Electrode

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### Abstract

An asymmetric diimine Schiff base, 2-((4-((2-hydroxybenzylidene)amino)benzylidene)amino) phenol (2-HBP), was covered to a glassy carbon (GC) electrode surface in nonaqueous medium to fabricate a modified electrode. Cyclic voltammetry was applied for the surface modification experiments in 1 mM diimine solution. Cyclic voltammetry, contact angle measurement, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy techniques were employed to characterize the modified GC (2-HBP-GC) surface. Electrochemical impedance results showed that the modified surface blocked the electron transfer with a 98.9% surface coverage value. Additionally, theoretical study was performed to gain insight into the structural and tautomeric aspects of the asymmetric diimine Schiff base. The phenol-imine and keto-amine tautomerism forms of the asymmetric diimine Schiff base were investigated by using DFT calculations.

## 1. INTRODUCTION

The electrode surface modification with a chemical compounds that contain heteroatom has become useful for analytical applications due to being high sensitive, selective, stable and economic. Additionally, they are easy to prepare and provide determination of low detection limit. Electrochemically modification of electrodes have advantages [1,2] in electrocatalysis [3,4], electron transfer kinetics [5,6], corrosion studies [7,8].

Schiff bases are significant chemical compounds that can be used for coating electrode surfaces. They contain an azomethine group. These ligands can bind transition metals and compose complexes. They are preferred to prepare modified electrodes owing to contain of amines and substituents on the aromatic rings [9].

Over the last few years, many researchers have interested in asymmetric Schiff bases. There are a lot of studies about Schiff bases and their metal complexes [10]. However, asymmetric Schiff bases have been rarely discussed [11-13]. There are some studies about electrochemical behavior of asymmetric Schiff bases [14-16], but we haven't yet seen any studies about their modification to electrode surface.

This study supports to prepare a modified surface by oxidation of 2-((4-((2-hydroxybenzylidene)amino)benzylidene)amino) phenol (2-HBP) on GC electrode. The cyclic voltammetry (CV), contact angle measurements (CAM), X-ray photoelectron spectroscopy (XPS) and

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electrochemical impedance spectroscopy (EIS) were used to clarify modified surface. These techniques have been efficiently applied to investigate the microscopic and spectroscopic properties of the coated surfaces.

The tautomeric preferences between the phenol-imine and keto-amine tautomer forms were discussed theoretically in the present paper. The relative abundances of the possible tautomer conformers were calculated. The phenol-imine and keto-amine tautomerisms of the asymmetric diimine Schiff base were investigated by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and UV-vis spectroscopies in our previous study [17]. In this paper we differently focused theoretically on the tautomerism in gaseous phase.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

Potassium ferrocyanide ( $\geq 99\%$ ), potassium ferricyanide ( $\geq 99\%$ ), potassium chloride (KCl; 99-100.5%), acetonitrile (ACN; 99.9%), ferrocene ( $\geq 98\%$ ), tetrabutylammonium tetrafluoroborate (TBATFB; 99%) were obtained from Merck and Sigma Aldrich. All chemicals used in this study were of analytical grade and don't need purification. All solutions were prepared at the concentration of 1mM in electrochemical and modification experiments. Ultra-pure water quality with a resistance of  $\sim 18.3 \text{ M}\Omega\cdot\text{cm}$  was used in all aqueous solutions and cleaning process of the electrodes. High purity nitrogen gas (99.999%) was used due to remove oxygen from the solution during the experiments. All experiments were carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ).

### 2.2. Apparatus

All electroanalytical measurements were performed with CHI 660B electrochemical Workstation. The experiments were practiced in a voltammetric cell using conventional three-electrode system containing glassy carbon (GC) electrode (BAS Model) as the working (geometric area is  $3 \text{ mm}^2$ ), an Ag/AgCl/KCl (sat.) used in aqueous media or an Ag/Ag $^+$  (0.01M) used in acetonitrile (ACN) as the reference and platinum wire as the counter electrodes.

Contact angle measurements were performed using Krüss DSA100 system. EIS measurements were carried out in the presence of a 1.0 mM ferrocyanide / 1.0 mM ferricyanide (1/1) mixture containing 0.1 M KCl. EIS measurements were performed from 100 kHz to 0.05 Hz using an AC amplitude set in 5 mV and at a DC potential of 0.215 V.

Thermo K-Alpha spectrometer equipped with Al K $\alpha$  X-rays (monochromatic) was used for the XPS results. It is realized out at  $90^\circ$  electron take-off angle. The pressures were kept below  $10^{-7}$  mbar during the experiments.

### 2.3. Computational Details

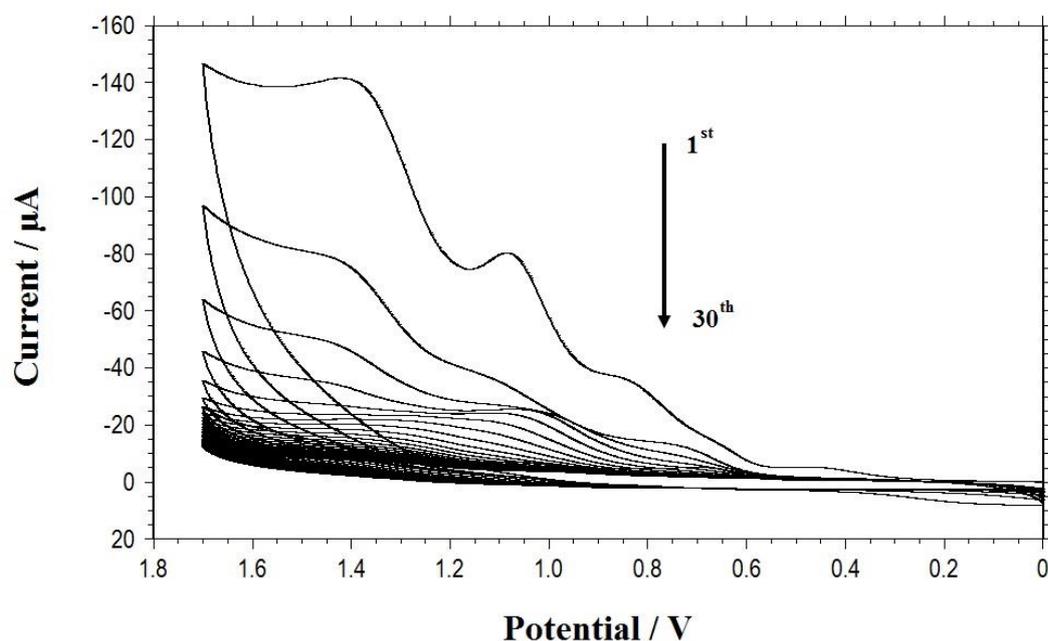
The possible conformations of the tautomers were determined by the relaxed PES scan for two dihedral angles, C6-C8-C11-N12 and N26-C27-C29-C31. The PES scan was performed in  $10^\circ$  intervals in the range  $0-360^\circ$  at the HF level, with the 6-31G(d) basis set. The possible conformers of four tautomeric forms of the asymmetric diimine Schiff base were fully optimized at the B3LYP/6-311 + G(d,p) level. All the computations were performed using Gaussian 09 program [18].

### 2.4. Cleaning of GC Electrode Surfaces

GC electrode was manually polished first with emery papers (Buehler) and then with 0.05  $\mu\text{m}$  alumina slurry (Baikowski Int. Corp.) on a microcloth pad (Buehler). Polished GC electrode was firstly cleaned by sonication in ultra-pure water and then in ACN for 10 min. for removal of alumina from the surface. Finally, GC electrode was rinsed with ACN.

## 2.5. 2-HBP-GC Electrode Preparation

The GC electrode surface coating process was practiced in 2-HBP solution (1mM) (synthesized procedure was given in reference [17]), in supporting electrolyte which is an ACN containing 0.1 M TBATFB. The CV technique was used with a sweep rate of  $100 \text{ mV s}^{-1}$  vs.  $\text{Ag}/\text{Ag}^+$  (0.01 M) reference electrode for 30 cycles from 0 V to 1.7 V to cover GC electrode [19,20]. After coating, the electrode was rinsed with ACN to purify materials from the electrode surface that physisorbed or unreacted. Figure 1 shows that while the number of CV cycles increases, the currents of anodic peaks decrease and reach a steady state value after 30 cycles.



**Figure 1.** The coating CVs of 1mM 2-HBP solution on GC electrode vs.  $\text{Ag}/\text{Ag}^+$ . 0.1 M TBATFB in acetonitrile was used as a supporting electrolyte and sweep rate is  $100 \text{ mV s}^{-1}$

The surfaces passivation process by the modification is also important for the prevent or minimize corrosive effects against the materials [21].

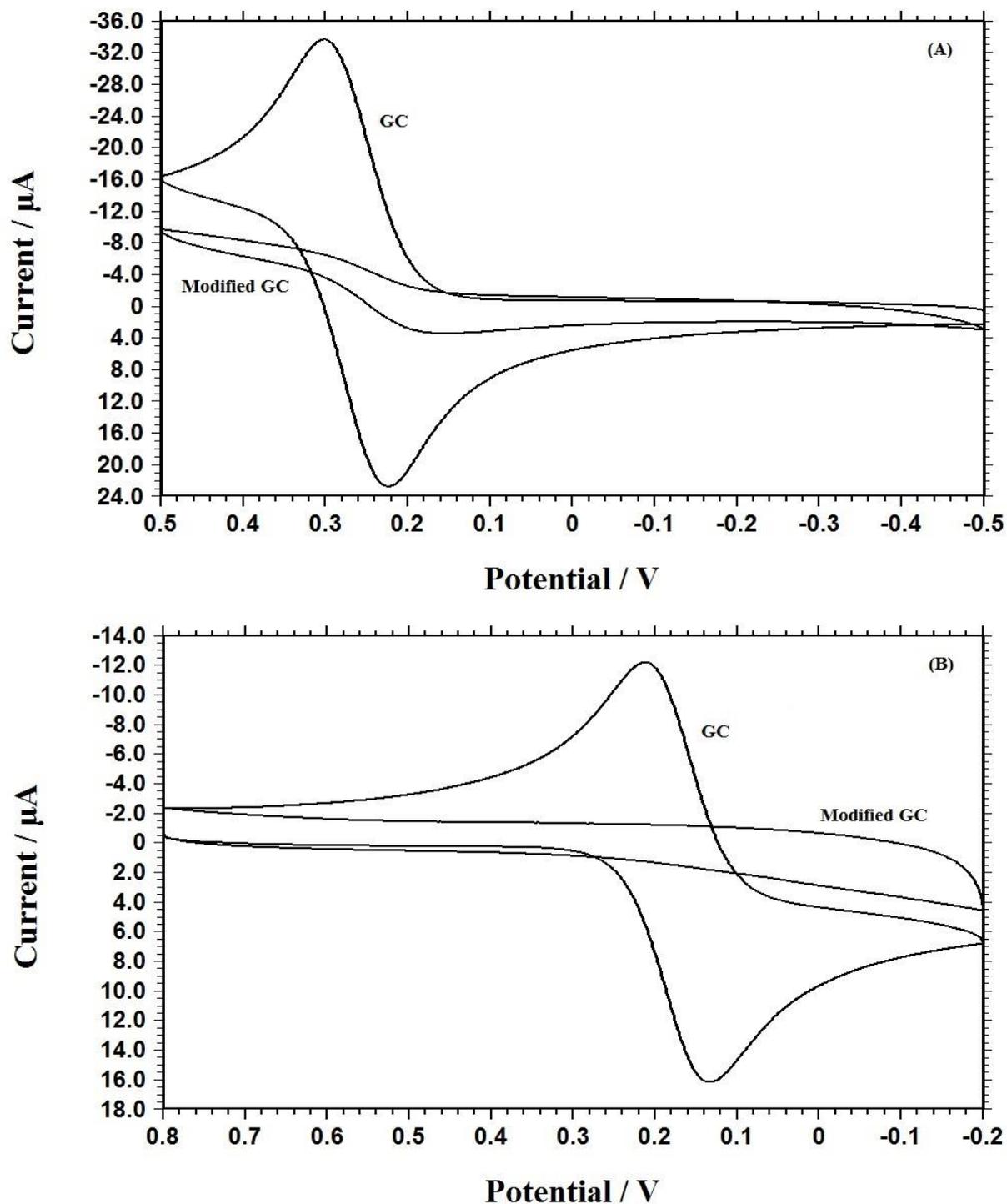
During anodic scan, two oxidation peaks were observed for 2-HBP at around 1.1 and 1.35 V, respectively. This should be attributed to the oxidation of hydroxy (OH) groups present on the 2-HBP molecule [22,23]. A decrease in peaks' currents was observed in following cycles for 2-HBP presumably because the OH group was converted to a free radical and stabilized by C-O-C coupling at the electrode surface [24,25].

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical Characterization of 2-HBP-GC Surface by CV

The electrochemical characterization of the proposed modified GC was performed using redox probes of ferrocene and ferricyanide. For comparison, the cyclic voltammograms (CVs) of the bare and 2-HBP-GC with redox active molecules in solution were analyzed. Figure 2 shows that the redox probes' peaks were

disappeared. This is because the 2-HBP-GC electrode blocked the heterogeneous electron transfer rate of redox probes [26].



**Figure 2.** CVs of 1 mM redox probes of (A) ferrocene (in acetonitrile containing 0.1 M TBATFB) vs. Ag/Ag<sup>+</sup> and (B) ferricyanide (in 0.1 M KCl) vs. Ag/AgCl/KCl (sat.) on bare GC and diimine-GC electrodes, sweep rate is 100 mV s<sup>-1</sup>

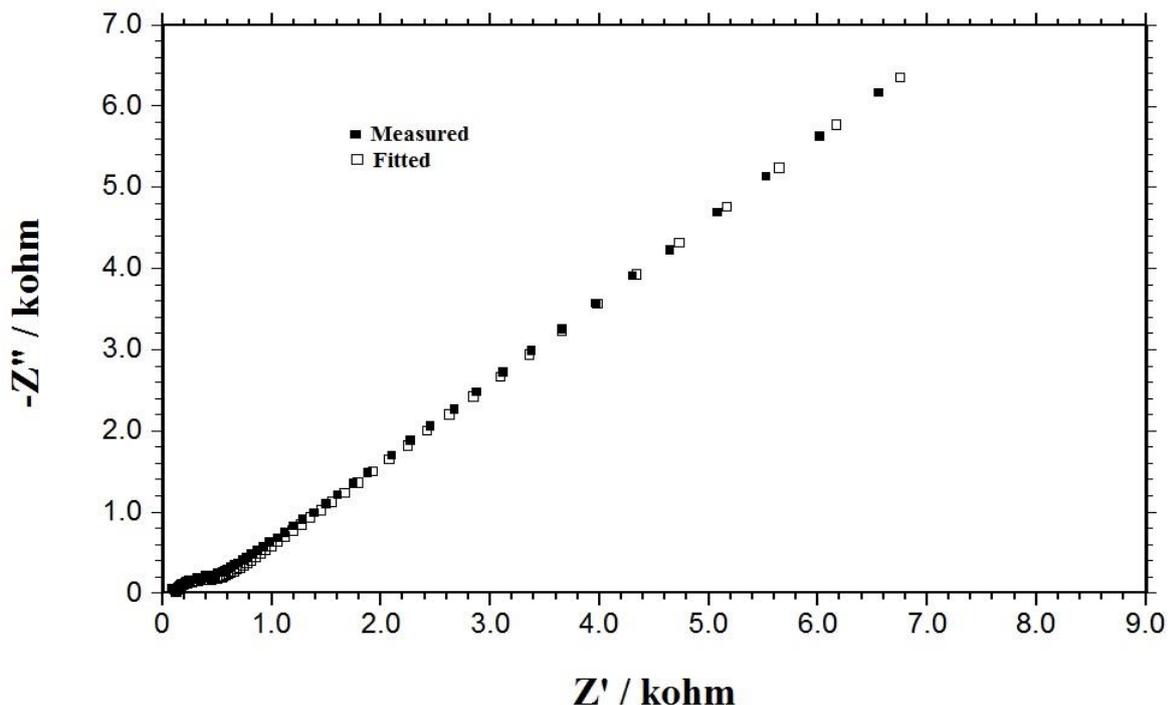
### 3.2. EIS Measurements

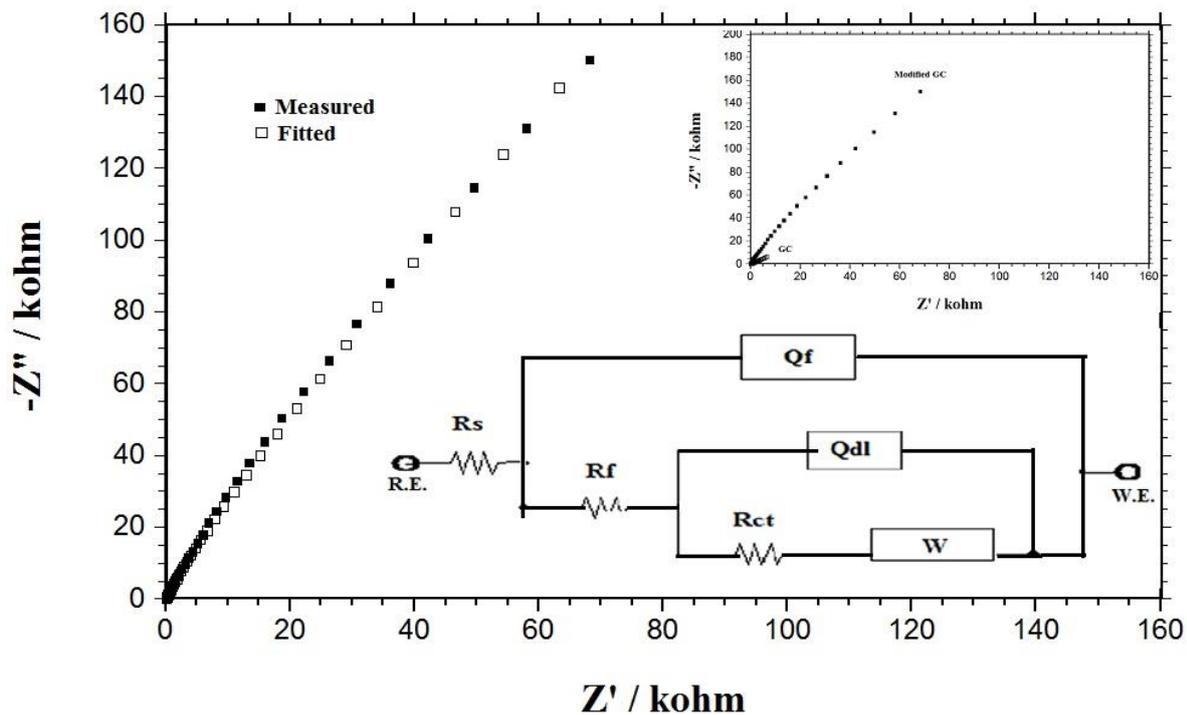
In an attempt to evince the differences among the electrochemical performance of the GC and 2-HBP-GC, EIS was used as an effective method for the characterization of each surface [27].

EIS was used for studying interfacial properties between electrode and solution. To assess the activity of 2-HBP-GC electrode, the ferrocyanide/ferricyanide couple (1 mM in 0.1 M KCl supporting electrolyte) was employed as a redox probe in EIS measurements at the open circuit potential. An equivalent circuit were used to fit the measured EIS data. The Nyquist plots of the redox couple on GC and 2-HBP-GC surface are shown in Figure 3(a) and Figure 3(b) with the equivalent electrical circuit model at the diimine modified surface. This equivalent circuit consists following parameters:  $R_s$ , a solution resistance,  $Q_f$ , a film capacitance,  $R_f$ , a coating resistance,  $Q_{dl}$ , a double layer capacitance,  $R_{ct}$ , a charge-transfer resistance and  $w$ , a Warburg impedance. The impedance spectra was fitted with this equivalent circuit and the values of  $Q_{dl}$  and  $R_{ct}$  were found [28,29].

As can be seen, the Nyquist curves for bare GC and coated surface are differ from each other. The Nyquist plot showed a Warburg line at the low frequency region which is the property of diffusional limiting electrochemical process with a small semicircle at the high frequency region on GC surface [30]. At the modified electrode the Nyquist plot exhibited a nearly straight line. The  $R_{ct}$  for the modified GC electrode is 34.6 k $\Omega$ , which is higher than the  $R_{ct}$  for bare GC electrode (0.374 k $\Omega$ ). The  $R_{ct}$  was increased because the diimine film blocked the access of ferrocyanide/ferricyanide to the electrode surface [31]; because of the large steric hindrance [32]. Also, the surface may be negatively charged and repulse the ferrocyanide/ferricyanide ions electrostaticly [33].

$\theta = 1 - R_{ct}^0 / R_{ct}$  equation was applied to calculate the electrode coverage degree [34]. In this equation,  $\theta$  is the surface coverage,  $R_{ct}^0$  is the charge transfer resistance for the bare GC electrode and  $R_{ct}$  is the charge transfer resistance for the 2-HBP-GC electrode. From this equation, the electrode surface coverage was calculated as 98.9%. This result may show that permeability of the modified electrode is low due to GC surface is coated with diimine film.





**Figure 3.** EIS at (a) bare GC and (b) 2-HBP-GC in  $1 \text{ mM Fe(CN)}_6^{3-/4-}$  containing  $0.1 \text{ M KCl}$ . For 2-HBP-GC electrode, the Randle's equivalent circuit model was given in Fig. 3(b) (at the bottom on the right hand side). Data were measured at  $5 \text{ mV}$  wave amplitude at  $0.215 \text{ V}$ , a formal potential, from  $100 \text{ kHz}$  to  $0.05 \text{ Hz}$

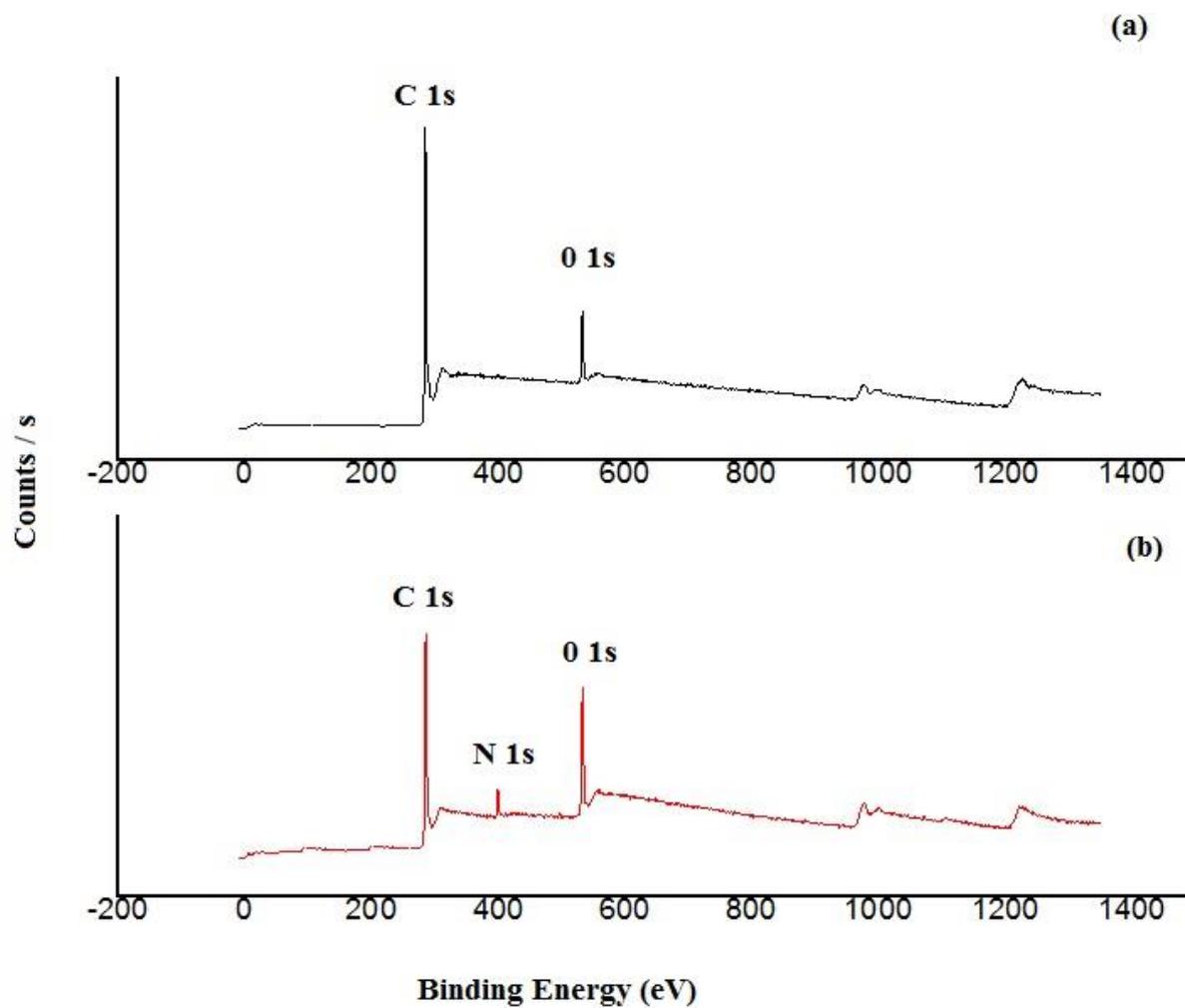
### 3.3. X-ray Photoelectron Spectroscopy Characterization of 2-HBP-GC Electrode

XPS analysis was carried out to learn about surface chemical compositions before and after modification [35]. The results were exhibited in Figure 4 for bare GC and modified GC electrodes. Figure 4(b) depicts the survey spectrum of XPS bands for C1s (285.2 eV), N1s (399.3 eV) and O1s (532.8 eV) elements on the 2-HBP-GC surface. The C1s and O1s peaks were observed on the bare GC surface (Figure 4(a)). O1s peak apparent on the bare GC surface is probably because of the surface preparing process [36]. After the electrochemical process, a N 1s signal at about 399.3 eV was observed in the XPS spectra of the modified GC electrode. The presence of the N 1s signal, moreover, increasing and decreasing of the percentage of O1s and C1s peak, respectively, demonstrates that the heteroaromatic molecules are on the GC surface.

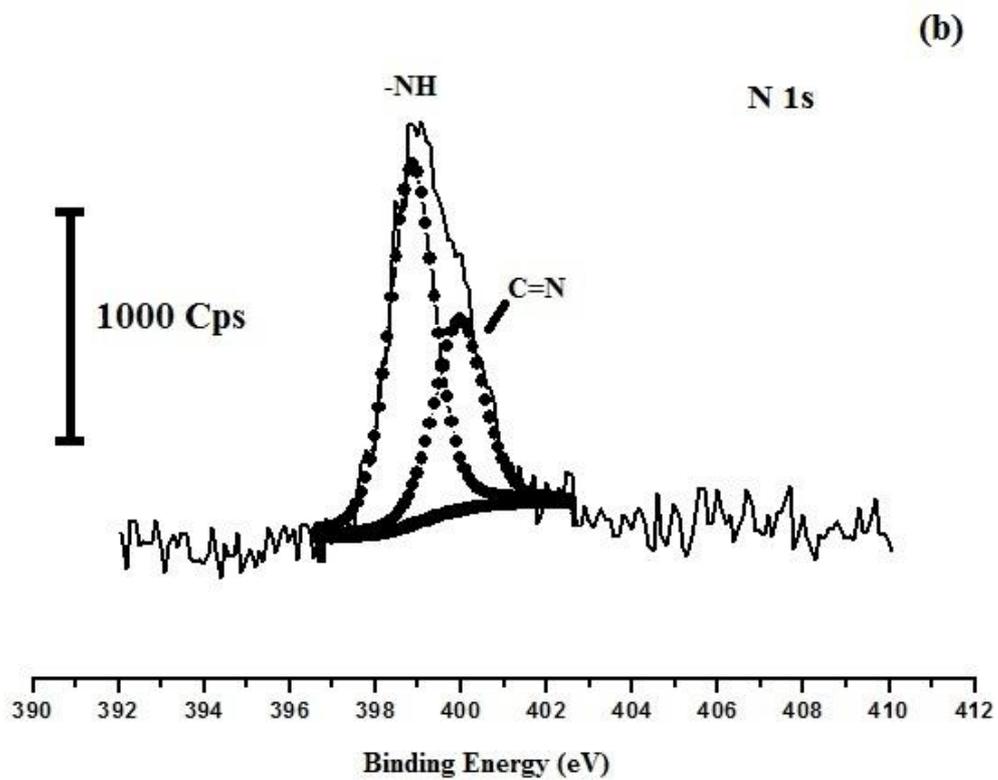
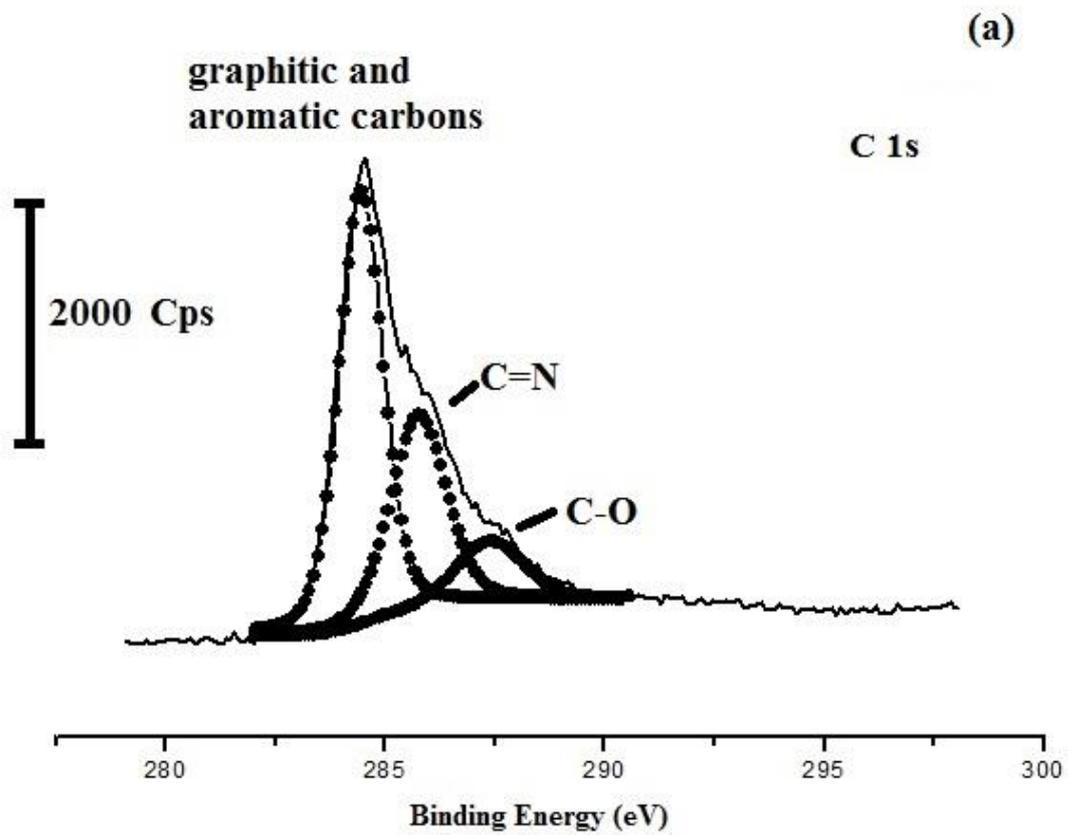
The C1s spectrum (Figure 5a) was deconvoluted into three peaks: graphitic and aromatic carbons at 284.5 eV [37,38], carbon in C=N bond belong to imine group at 285.8eV, and C-O bond in phenolic group at 287.4 eV [39].

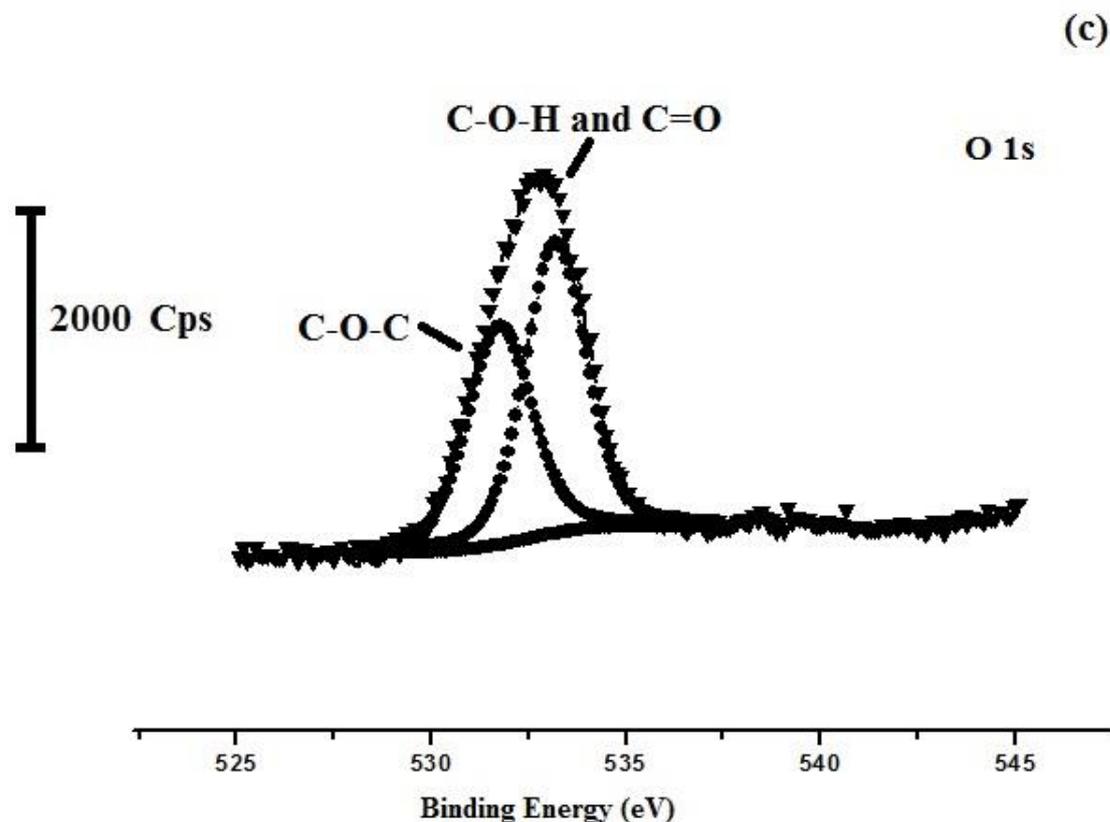
The N 1s spectrum of 2-HBP-GC exhibited two peaks at 398.9 eV and 400.0 eV binding energies (Figure 5b), which can be assigned to the NH in tautomeric amino groups and the C=N [40] in imine groups.

The peak spectrum of O1s (Figure 5c) was fitted with two components. The peak centred at about 531.7 eV probably indicates a mixture of oxygen atoms in hydroxyl (C-O-H) [41] and C=O bonds [37] due to keto-amine tautomer form. The band was detected at about 533 eV belongs to oxygen from C-O-C [42].



**Figure 4.** Survey spectra of XPS for the (a) bare GC and (b) 2-HBP-GC surfaces





**Figure 5.** XPS spectras for the (a) C 1s, (b) N 1s and (c) O 1s peaks on the dimine-GC surfaces

### 3.4. Contact Angle Measurements

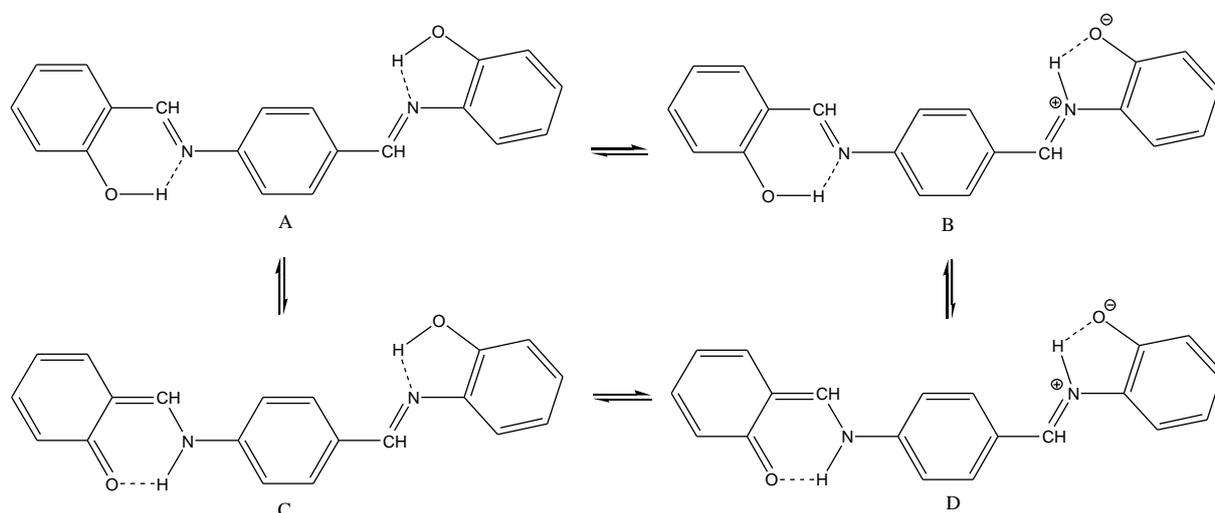
The contact angle (CA) is a sensitive method to identify wettability [43]. The CA is used to investigate the polarity of the surface and also the hydrophilic and heterogenic features of surface [44]. The water CA measurements were measured at room temperatures. A Kruss, DSA100, Germany system was used (a drop shape analysis system) coupled with a Peltier element. The volume of the deionized water droplet is 1  $\mu$ L. The equilibrium CA of deionized water was found as  $86^{\circ} \pm 1^{\circ}$  on GC surface and  $75^{\circ} \pm 1^{\circ}$  on the 2-HBP-GC surface. This differentiation in the value of the CA gives information about hydrophobic/hydrophilic character of the surface. This CA value for the 2-HBP-GC surface, which was nearly  $10^{\circ}$  smaller than bare GC confirms that the surface was modified; it also demonstrates that the 2-HBP-GC surface is more hydrophilic than the GC surface, as awaited, due to the hydroxyl groups in Schiff base. This relatively hydrophilic surface is beneficial for the determination of hydrophilic species as a tool.

### 3.5. Structure and Tautomerism

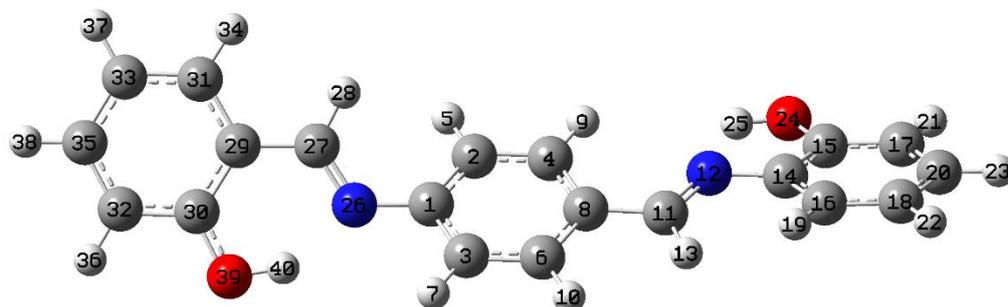
The structure of the diimine Schiff base with numbering scheme for the atoms is presented in Figure 7. Selected optimized geometric parameters at B3LYP with 6-311+G(d,p) basis set are given in Table 1. All the possible tautomers are given in Figure 6 and they have C1 symmetry. 2-HBP has four possible tautomeric forms, namely A (phenol-imine/phenol-imine), B (phenol-imine/keto-amine), C (phenol-imine/zwitter ion) and D (keto-amine/zwitter ion).

The phenol-imine/phenol-imine tautomeric form (A) contains salicyldiimine fragment as six-membered chelate ring (left side) formed by intramolecular hydrogen bonding feature between the H40 and N26 atoms with a bond length of 1.740 Å. Salicyldiimine fragment twisted with a torsion angles of  $-34.98^{\circ}$  to the phenyl ring. The phenol-imine/phenol-imine tautomeric form contains phenylazomethine fragment (right side) as a five-membered chelate ring formed by (O24-H25. . .N12) type intramolecular hydrogen

bond with a bond length of 2.077 Å. The phenylazomethine fragment is nearly planar to the phenyl ring with a torsion angle of  $-2.82^\circ$ . The keto-amine/phenol-imine tautomeric form (B) is nearly planar. The phenylazomethine fragment twisted  $4.52^\circ$  to the phenyl ring and salicyldiimine fragment twisted  $-1.67^\circ$  to the phenyl ring. DFT quantum chemical calculations showed that the tautomer A (phenol-imine/phenol-imine) is the most stable species in the gas phase. The most stable conformation of the tautomer A is shown in Figure 7 with atomic numbering.



**Figure 6.** Possible tautomeric forms of the 2-HBP



**Figure 7.** The optimized geometry of the most stable tautomeric form A (phenol-imine/phenol-imine) of the 2-HBP

**Table 1.** Calculated structural parameters (bond length in Å, angles in degree) of the 2-HBP.

Parameter	Tautomers				Parameter	Tautomers			
Bond lengths	A	B	C	D	Bond angles	A	B	C	D
C29-C27	1.448	1.446	1.397	1.397	C29-C27-N26	122.40	122.39	122.13	121.93
C27-N26	1.295	1.297	1.335	1.337	C27-N26-C1	121.44	121.70	128.58	128.71
N26-C1	1.404	1.400	1.400	1.395	C4-C8-C11	122.39	123.81	122.38	123.89
C8-H11	1.462	1.441	1.462	1.440	C11-N12-C14	122.47	132.85	122.42	132.87
C11-N12	1.286	1.314	1.286	1.315	N12-C14-C15	114.42	110.68	114.50	110.64
N12-C14	1.403	1.378	1.403	1.377	C14-C15-O24	119.79	119.53	119.83	119.49
C15-O24	1.357	1.264	1.357	1.264	Torsion angles				
C14-C15	1.416	1.462	1.416	1.463	C31-C29-C27-N26	179.34	179.10	-180.00	-180.00
C29-C31	1.412	1.413	1.432	1.432	C29-C27-N26-C1	177.01	176.68	-179.98	-180.00
C2-C4	1.388	1.386	1.387	1.385	C27-N26-C1-C3	147.26	149.40	178.55	-179.97
O39-H40	1.357	0.996	-	-	C6-C8-C11-N12	176.63	-179.79	-175.67	180.00
O24-H25	0.976	-	0.976	-	C11-N12-C14-C15	162.54	-179.87	-161.26	180.00

Tautomerism of the 2-HBP was investigated theoretically. The total energies, relative energies and mol fractions of tautomers of the asymmetric diimine Schiff base are given in Table 2. The relative abundances of the possible tautomers A, B, C and D were calculated using the Boltzmann distribution equation. According to the calculation results the asymmetric diimine Schiff exists completely in phenol-imine/phenol-imine tautomeric form (A) as expected because intramolecular O-H...N bonds stabilizes this form.

The experimental results showed that the 2-HBP existed in completely phenol-imine/phenol-imine tautomeric form (A) in solid state and solutions [17]. Theoretical results showed that the 2-HBP existed in tautomeric form A in gaseous phase, too.

**Table 2.** The total energies, relative energies and mol fractions of tautomers of the 2-HBP.

Tautomer	Total energy (a.u.)	Relative energy (kJ/mol)	Mol fractions of tautomers
A	-1031.784231	0.00	1.0
B	-1031.762312	57.55	0.0
C	-1031.776905	19.75	0.0
D	-1031.754565	77.89	0.0

#### 4. CONCLUSION

A new asymmetric diimine Schiff base modified GC electrode was fabricated by the electrochemical oxidation method using CV. This simple and cost-effective surface was characterized by different techniques such as CV, EIS, XPS and CAM. EIS results show that the charge transfer resistance of the 2-HBP-GC surface for probe ions increased greatly with a high surface coverage (98.9%). The higher Rct value shows that the surface is more compact and less permeable. XPS was fundamentally used for the specify of chemical bonding in the structure of diimine which were coated to the GC surface. We expect that this novel surface can be used in the protecting the materials against corrosion also separation and detection of biological or ionic samples. DFT calculation results showed phenol-imine/phenol-imine tautomer is the most stable tautomeric form in gaseous form.

#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

**REFERENCES**

- [1] Saghatforoush, L., Hasanzadeh M., Shadjou N., Khalilzadeh, B., “Deposition of new thia-containing Schiff-base iron (III) complexes onto carbon nanotube-modified glassy carbon electrodes as a biosensor for electrooxidation and determination of amino acids”, *Electrochimica Acta*, 56: 1051-1061, (2011).
- [2] Abbaspour, A., Ghaffarinejad, A., “Electrocatalytic oxidation of l-cysteine with a stable copper–cobalt hexacyanoferrate electrochemically modified carbon paste electrode”, *Electrochimica Acta*, 53: 6643-6650, (2008).
- [3] Shi, F., Xi, J., Hou, F., Han, L., Li, G., Gong, S., Chen, C., Sun, W., “Application of three-dimensional reduced graphene oxide-gold composite modified electrode for direct electrochemistry and electrocatalysis of myoglobin”, *Materials Science and Engineering C*, 58: 450-457, (2016).
- [4] Umasankar, Y., Prakash, Periasamy, A., Chen, S.-M., “Electrocatalysis and simultaneous determination of catechol and quinol by poly(malachite green) coated multiwalled carbon nanotube film”, *Analytical Biochemistry*, 411: 71-79, (2011).
- [5] Losada, J., García Armada, M. P., García, E., Casado, C.M., Alonso, B., “Electrochemical preparation of gold nanoparticles on ferrocenyl-dendrimer film modified electrodes and their application for the electrocatalytic oxidation and amperometric detection of nitrite”, *Journal of Electroanalytical Chemistry*, 788: 14-22, (2017).
- [6] Lee, J.-Ho, Oh, B.-K., Choi, J.-W., “Electrochemical sensor based on direct electron transfer of HIV-1 Virus at Au nanoparticle modified ITO electrode”, *Biosensors and Bioelectronics* 49: 531-535, (2013).
- [7] Popović, M.M., Grgur, B.N., Mišković Stanković, V.B., “Corrosion studies on electrochemically deposited PANI and PANI/epoxy coatings on mild steel in acid sulfate solution”, *Progress in Organic Coatings*, 52: 359-365, (2005).
- [8] Peulon, S., Antony, H., Legrand, L., Chausse, A., “Thin layers of iron corrosion products electrochemically deposited on inert substrates: synthesis and behaviour”, *Electrochimica Acta*, 49: 2891-2899, (2004).
- [9] Siqueira de Oliveira, L., Balbino, M.A., Teles de Menezes, M.M., Dockal, E.R., Firmino de Oliveira, M., “Voltammetric analysis of cocaine using platinum and glassy carbon electrodes chemically modified with Uranyl Schiff base films”, *Microchemical Journal*, 110: 374-378, (2013).
- [10] Neelakantan, M.A., Rusalraj, F., Dharmaraja, J., Johnsonraja, S., Jeyakumar, T., Sankaranarayana Pillai, M., “Spectral characterization, cyclic voltammetry, morphology, biological activities and DNA cleaving studies of amino acid Schiff base metal(II) complexes”, *Spectrochimica Acta Part A*, 71: 1599-1609, (2008).
- [11] Jancsó, A., Paksi, Z., Mikkola, S., Rockenbauer, A., Gajda, T., “Iron(III) and copper(II) complexes of an asymmetric, pentadentate salen-like ligand bearing a pendant carboxylate group”, *Journal of Inorganic Biochemistry*, 99: 1480-1489, (2005).

- [12] Kasumov, V.T., Köksal, F., “Synthesis, spectroscopy, and electrochemistry of copper(II) complexes with *N,N*-bis(3,5-di-*t*-butylsalicylideneimine) polymethylenediamine ligands”, *Spectrochimica Acta Part A*, 61: 225-231, (2005).
- [13] Khorshidifard, M., Rudbari, H.A., Kazemi-Delikani, Z., Mirkhani, V., Azadbakh, R., “Synthesis, characterization and X-ray crystal structures of Vanadium(IV), Cobalt(III), Copper(II) and Zinc(II) complexes derived from an asymmetric bidentate Schiff-base ligand at ambient temperature”, *Journal of Molecular Structure*, 1081: 494-505, (2015).
- [14] Güngör, S.A., Köse, M., Tümer, F., Tümer, M., “Photoluminescence, electrochemical, SOD activity and selective chemosensor properties of novel asymmetric porphyrin-Schiff base compounds”, *Dyes and Pigments*, 130: 37-53, (2016).
- [15] Anbu, S., Kandaswamy, M., Suthakaran, P., Murugan, V., Varghese, B., “Structural, magnetic, electrochemical, catalytic, DNA binding and cleavage studies of new macrocyclic binuclear copper(II) complexes”, *Journal of Inorganic Biochemistry*, 103: 401-410, (2009).
- [16] Habibi, M.H., Mikhak, M., “Synthesis, spectral, photolysis and electrochemical studies of mononuclear copper(II) complex with a new asymmetric tetradentate ligand: Application as copper nanoparticle precursor”, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 96: 501-505, (2012).
- [17] Güngör, Ö., Gürkan, P., “Synthesis and spectroscopic properties of novel asymmetric Schiff bases”, *Spectrochimica Acta Part A*, 77: 304-311, (2010).
- [18] Frisch, M.J., Trucks, G.W., Schlegel, H.B. et al., “Gaussian 09, Revision A.02”, Gaussian Inc, Wallingford, Conn, USA, (2009).
- [19] Siqueira de Oliveira, L., Balbino, M.A., Teles de Menezes, M.M., Dockal E.R., Firmino de Oliveira, M., “Voltammetric analysis of cocaine using platinum and glassy carbon electrodes chemically modified with Uranyl Schiff base films”, *Microchemical Journal*, 110: 374-378, (2013).
- [20] Praveen Kumar, S., Giribabu, K., Manigandan, R., Munusamy, S., Muthamizh, S., Padmanaban, A., Dhanasekaran, T., Suresh, R., Narayanan, V., “Simultaneous determination of paracetamol and 4-aminophenol based on poly(chromium Schiff base complex) modified electrode at nanomolar levels”, *Electrochimica Acta*, 194: 116-126, (2016).
- [21] Escobar, C., Caicedo, J.C., Aperador, W., Delgado, A., Prieto, P., “Improve on Corrosion Resistant Surface for AISI 4140 Steel Coated with VN and HfN Single Layer Films”, *International Journal of Electrochemical Science*, 8: 7591-7607, (2013).
- [22] Tsai, F.C., Chang, C.C, Liu, C.L., Chen, W.C., Jenekhe, S.A., “New thiophene-linked conjugated poly(azomethine)s: Theoretical electronic structure, synthesis, and properties”, *Macromolecules*, 38: 1958-1966, (2005).
- [23] Kaya, İ., Bora, E., Aydın, A., Synthesis and characterization of Schiff base derivative with pyrrolering and electrochromic applications of its oligomer, *Progress in Organic Coatings*, 77: 463-472, (2014).

- [24] Rauf, A., Shah, A., Khan, A.A., Shah, A. H., Abbasi, R., Qureshi, I.Z., Ali, S., Synthesis, pH dependent photometric and electrochemical investigation, redox mechanism and biological applications of novel Schiff base and its metallic derivatives, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 176: 155-167, (2017).
- [25] Kaya İ., Yıldırım, M., Aydın, A., Şenol, D., Synthesis and characterization of fluorescent graft fluorene-co-polyphenol derivatives: The effect of substituent on solubility, thermal stability, conductivity, optical and electrochemical properties, *Reactive & Functional Polymers*, 70: 815-826, (2010).
- [26] Saby, C., Ortiz, B., Champagne, G.Y., Bélanger, D., “Electrochemical Modification of Glassy Carbon Electrode Using Aromatic Diazonium Salts. 1. Blocking Effect of 4-Nitrophenyl and 4-Carboxyphenyl Groups”, *Langmuir*, 13: 6805-6813, (1997).
- [27] Sanghavi, B.J., Kalambate, P.K., Karna, S.P., Srivastava, A.K., “Voltammetric determination of sumatriptan based on a graphene/gold nanoparticles/Nafion composite modified glassy carbon electrode”, *Talanta*, 120: 1-9, (2014).
- [28] Uzun, D., Arslan, H., Balaban Gündüzalp, A., Hasdemir, E., “Preparation of modified glassy carbon surface with N-(1-H-indole-3yl)methylene thiazole-2-amine and its characterization”, *Surface and Coatings Technology*, 239: 108-115, (2014).
- [29] Zheludkevich, M.L., Yasakau, K.A., Poznyak, S.K., Ferreira, M.G.S., “Triazole and thiazole derivatives as corrosion inhibitors for AA2024 aluminium alloy”, *Corrosion Science*, 47: 3368-3383, (2005).
- [30] Li, M., Jing, L., “Electrochemical behavior of acetaminophen and its detection on the PANI-MWCNTs composite modified electrode”, *Electrochimica Acta*, 52: 3250-3257, (2007).
- [31] Hashkavayi, B.A., Raouf, J.B., “Design an aptasensor based on structure-switching aptamer on dendritic gold nanostructures/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/DABCO modified screen printed electrode for highly selective detection of epirubicin”, *Biosensors and Bioelectronics*, 91: 650-657, (2017).
- [32] Surucu, O., Bolat, G., Abaci, S., “Electrochemical behavior and voltammetric detection of fenitrothion based on a pencil graphite electrode modified with reduced graphene oxide (RGO)/poly(E)-1-(4-((4-(phenylamino)phenyl)diazenyl)phenyl)ethanone (DPA) composite film”, *Talanta*, 168: 113-120, (2017).
- [33] Chen, J., Huang, B., Zhan, S., Ye, J., “A trinuclear copper(I) complex modified Au electrode based on a nonelectrocatalytic mechanism as hydrogen peroxide sensor”, *Journal of Electroanalytical Chemistry*, 759: 194-200, (2015).
- [34] Zhang, R., Jin, G.-D., Chen, D., Hu, X.-Y., “Simultaneous electrochemical determination of dopamine, ascorbic acid and uric acid using poly(acid chrome blue K) modified glassy carbon electrode”, *Sensors and Actuators B*, 138: 174-181, (2009).
- [35] Singh, B., Diwan, A., Jain V., H.-G.A., Terry, J., Linford, M.R., “Uniqueness plots: A simple graphical tool for identifying poor peakfits in X-ray photoelectron spectroscopy”, *Applied Surface Science*, 387: 155-162, (2016).
- [36] Uzun, D., Balaban Gündüzalp, A., Hasdemir, E., “Selective determination of dopamine in the presence of uric acid and ascorbic acid by N,N'-bis(indole-3-carboxalimine)-1,2-

- diaminocyclohexane thin film modified glassy carbon electrode by differential pulse voltammetry”, *Journal of Electroanalytical Chemistry*, 747: 68-76, (2015).
- [37] Tavenner, E., Meredith, P., Wood, B., Curry, M., Giedd, R., “Tailored conductivity in ion implanted polyetheretherketone”, *Synthetic Metals*, 145: 183-190, (2004).
- [38] Sandrin, L., Sacher, E., “X-ray photoelectron spectroscopy studies of the evaporated aluminum/ corona-treated polyethylene terephthalate interface”, *Applied Surface Science*, 135: 339-349, (1998).
- [39] Tze, W. T.Y., Bernhardt, G., Gardner, D. J., Christiansen, A.W., “X-ray photoelectron spectroscopy of wood treated with hydroxymethylated resorcinol”, *International Journal of Adhesion & Adhesives*, 26: 550-554, (2006).
- [40] Onoa, G.B., Moreno, V., “Palladium and platinum famotidine complexes”, *Journal of Inorganic Biochemistry*, 72: 141-153, (1998).
- [41] Xu, X., Wang, L., Guo, S., Lei, L., Tang, T., “Surface chemical study on the covalent attachment of hydroxypropyltrimethyl ammonium chloride chitosan to titanium surfaces”, *Applied Surface Science*, 257: 10520-10528, (2011).
- [42] Vinu, A., Anandan, S., Anand, C., Srinivasu, P., Ariga, K., Mori, T., “Fabrication of partially graphitic three-dimensional nitrogen-doped mesoporous carbon using polyaniline nanocomposite through nanotemplating method”, *Microporous and Mesoporous Materials*, 109: 398-404, (2008).
- [43] Lu, X., Liu, J., Xu, X., “Contact angle measurements of pure refrigerants”, *International Journal of Heat and Mass Transfer*, 102: 877-883, (2016).
- [44] Grundke, K., Werner, C., Pöschel, K., Jacobasch, H.-J., “Characterization of adsorbed protein layers by low-rate dynamic liquid–fluid contact angle measurements using axisymmetric drop shape analysis (part II)”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 156: 19-31, (1999).