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# Covalently Grafted on to the Glassy Carbon Electrode in Non-Aqueous Media of Apigenin and Naringenin as Different Flavonoid Derivatives

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**Abstract**- In this paper, *apigenin* (AG) and *naringenin* (NG) have been studied with the cyclic voltammetric technique using the glassy carbon (GC) electrode. The modification was carried out only in non-aqueous media, while the electrochemical characterization was done in both aqueous and non-aqueous media. 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile (MeCN) was used in non-aqueous experiments, Britton-Robinson (BR) buffer solution (pH=2) and 0.1 M KCl solution were used in aqueous experiments. Surface modification experiments were performed in the +0.3 V and +2.8 V potential ranges with a scan rate of 0.1 $Vs^{-1}$ and 10 cycles for two molecules. The presence of AG and NG at the GC electrode surface was characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), contact angle measurement (CAM) technique and atomic force microscopy (AFM). We also investigated the electrochemical oxidation of AG and NG in non-aqueous media and propose a grafting mechanism of AG and NG to the GC electrode surface.

**Keywords**- Flavonoid, Electrochemical Oxidation, Surface Modification, Surface Characterization

## 1. INTRODUCTION

Flavonoids are a group of aromatic, oxygen-containing heterocyclic pigments widely distributed among higher plants as secondary metabolites. The chemical structure of flavonoids having more than 8000 derivatives today is based on a $C_{15}$ skeleton which consists of two phenyl rings and a heterocyclic ring [1]. Flavonoids are broken down into categories of flavones, flavonols, isoflavones, anthocyanidins, flavans and flavanones [2]. Flavonoids constitute one of the most characteristic classes of compounds containing hydroxyl groups attached to ring structures [3]. Many flavonoids are easily recognised as flower pigments in most angiosperm families. However, their occurence is not restricted to flowers but include all parts of the plants. They constitute most of the yellow, red and blue colors in flowers and fruits. They generally display a chromophore of the 2-phenyl-1-benzopyran type diversely substituted by OH and OMe groups. Besides their important biological roles in plant pigmentation, nitrogen fixation and chemical defense, flavonoids possess anti-cancer, anti-viral and anti-inflammatory properties, which are the consequence of their affinity for proteins (including enzymes) and their antioxidant properties [4].

Electrochemical methods are based on the direct oxidation or reduction of substrate onto an electrode surface. Electrode reactions are very suitable for analytical applications due to their requirements of high potential. Moreover, these surfaces can be modified by a reductive substrate for analytical applications. Recently, the application of inorganic modified electrodes has increased [5-8]. Anodes, suitable for the active and high positive potentials are important for the electro-oxidation of organic pollutants. However, oxygen is 48 released at higher potential which interferes obtaining good results [9-11]. In the electro-oxidation, hydroxylation and hydrogen evolution take place which is a favored situation due to hydroxy adsorption [12, 13].

The above mentioned pertinent literature suggests very different electrochemical oxidation mechanism and electrochemical behaviors of quercetin and other flavonoids. Most of the authors tried to imply a relationship between electrochemical behavior and antioxidant capacity of flavonoids in aqueous and non-aqueous medium. The ease of electrochemical oxidation of a flavonoid is of importance for its antioxidant capacity. The rationale behind this idea is the assumption of the similar mechanism of electrochemical oxidation and free radical scavenging [14, 15].

Although, some correlation can be found between solution electrochemical behavior and antioxidant capacity, it is more realistic to find such a relation in solid state of these compounds. The study of solid state electrochemistry of flavonoids offers many advantages such as strong H-bonding and different isomerism. Solid-state electroanalysis of flavonoids can be investigated either by mechanical immobilization or by covalent grafting at the surface of carbon or metal electrodes. The former methodology, so called voltammetry of microparticles (VMP), presents some disadvantages as dissolution of immobilized molecules during electrochemical measurements and unknown amount of deposited microparticles at the electrode surface [16, 17]. Covalent grafting methods based on the amine oxidation [13]

aryl diazonium salt reduction [18] and oxidation in the presence of alcohols [19, 20] have been employed to derivative the surfaces of carbon and metals.

The aim of the present paper is concerned with the covalent modification of GC electrode with AG and NG which is barely cited in the literature as flavonoid derivatives in non-aqueous media by oxidation of these structurally related flavonoids at a GC electrode. The difference on the 2nd and 3rd position of carbon atom in the ring C is the main for choosing these two molecules. There is a double bond between these two positions in AG whereas there is only a single carbon-carbon bond. Beyond this difference the two molecules are structurally the same (Fig.1). This difference in structure deserves an electrochemical approach which was tired to be performed by using electrochemical and spectroscopic techniques to determine the similarities and the differences between the two molecules. In this study, we also investigate the electrochemical oxidation of flavonoids in non-aqueous media and the catalytic effect of flavonoids attached to the glassy carbon surface. In these experiments each step was tested by using electrochemical and spectroscopic techniques.

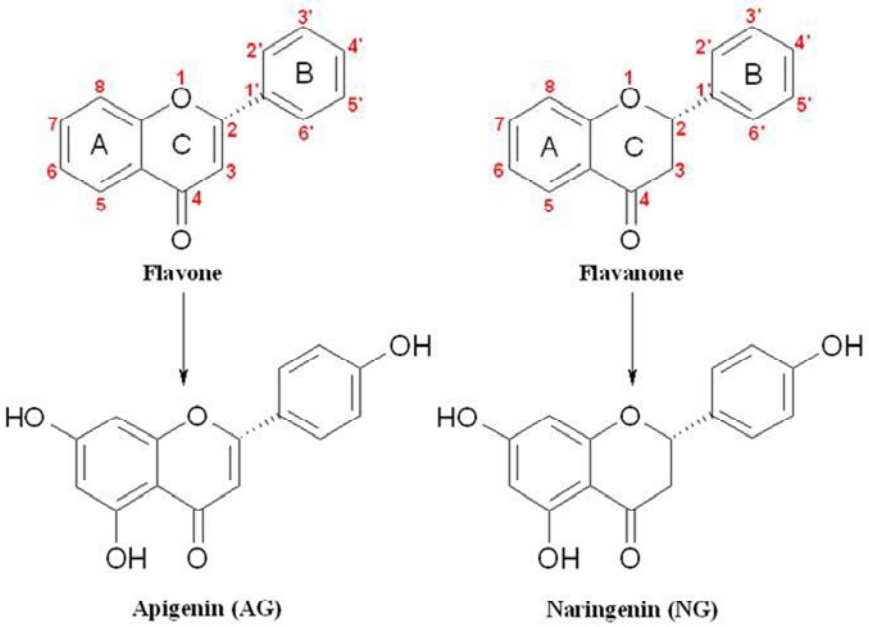


**Fig. 1.** Chemical structures of two flavonoids

## 2. EXPERIMENTAL

### 2.1. Reagents and chemicals

All chemicals were used as received without further purification from Fluka and Sigma-Aldrich. All chemicals were used as received of analytical-reagent grade supplied from Fluka and Sigma-Aldrich. The modification and characterization experiments were performed in

both aqueous and non-aqueous media. All flavonoid solutions used in modification were 1 mM concentration in MeCN containing 0.1 M, TBATFB as supporting electrolyte. Solutions were thoroughly deoxygenated by purging with purified argon gas (99.999%) for 10 min prior to the electrochemical experiments. Argon blanket was maintained over the solutions to supply an inert atmosphere during voltammetric measurements.

**2.2. Electrodes and apparatus**

Ultra pure quality of water with a resistance of 18.3 MΩ cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used in preparations of aqueous solutions, cleaning of the glassware and polishing the electrodes. All electrochemical and spectroscopic experiments were performed at room temperature (25±1 $^{o}$C). Electrochemical surface modification experiments were performed in the +0.3 V and +2.8 V potential ranges at a scan rate of 0.1 $Vs^{-1}$ with 10 cycles. A traditional three-electrode cell system was used in all electrochemical experiments. In our experiments, GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from Gamry Instruments (PA, USA) electrochemical analyzer with BAS (Bioanalytical Systems, West Lafayette, IN, USA) Model MF-2012 and Tokai GC-20 glassy carbon electrodes were used. $Ag/Ag^{+}$ (10 mM $AgNO_3$ in 0.1 M TBATFB) (BAS Model MF-2042) for non-aqueous media and a Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used as reference electrodes. Pt wire counter electrode (BAS Model MW-1032) was used. As a buffering media, Britton–Robinson (BR) solution was used for adjusting the pH of the solutions from 1.81 to 11.98 using Jenway 3010 pH meter.

CV and EIS techniques were performed using a GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA equipped with a BAS model C3 cell stand. The same electrochemical device and software were used for the both modification and process. Characterizations of the modified surfaces were recorded by electrochemical impedance spectroscopy (EIS), contact angle measurement (CAM) and atomic force microscopy (AFM) techniques. EIS experiments were carried out with a Gamry Reference PCI4/750 potentiostat in conjunction with EIS 300 software. EIS surface data were obtained in the 1 mM $Fe(CN)_6^{3-/4-}$ redox couple at the frequency range of 100.000–0.05 Hz at 10 mV wave amplitude.

The CAMs were carried out with a contact angle measuring system: G-III model Contact Angle Meter (Kernco Instrument Co. Inc. El Paso, TX) at 25 $^{o}$C. The sessile drop method was used to measure the contact angle and the drop was formed by depositing the liquid onto the GC electrode surface using a manual micro-syringe. Both the left and the right contact angles and drop dimension parameters were automatically calculated from the digitalized image. The reproducibility of contact angle results is in the range of ± 0.5º.

AFM experiments were recorded with a High Resolution Ambient MFM/AFM (Ankara, Turkey). The measurements were carried out at *Tapping* mode in a 1 μm×1 μm area.

### 2.3. Preparation of the working electrodes

GC electrodes were prepared for the modification experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with 1.0 μm and 0.3 μm alumina slurry on micro cloth pads (Buehler, USA). After the initial polishing, GC electrodes were resurfaced using 0.05 μm alumina slurry. First, GCs were sonicated in water and then in 1:1 (v/v) isopropyl alcohol and acetonitrile (IPA+MeCN) (Aldrich) mixture for 10 min. All of these steps were performed before the electrochemical experiments in order to avoid contamination of oxidation products and to obtain a clean renewed electrode surface [21].

### 2.4. Modification of GC electrodes

The electrochemical modification was performed in a conventional three-electrode system at room temperature. GC electrode surfaces after cleaning and polishing were dried with argon gas prior to modification. AG and NG solutions (1 mM) were prepared in 0.1 M TBATFB (in MeCN). The electrodes were then treated by CV in the potential range from +0.3 V to +2.8 V at a 0.1 $Vs^{-1}$ scan rate at 10 cycles for two molecules.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical oxidation in solution and chemical grafting of AG and NG onto the GC electrode surface

Two structurally different but related flavonoids, AG and NG (Fig. 2) were investigated electrochemically both in solution and in solid state attached to the GC electrode surface via covalent bond.

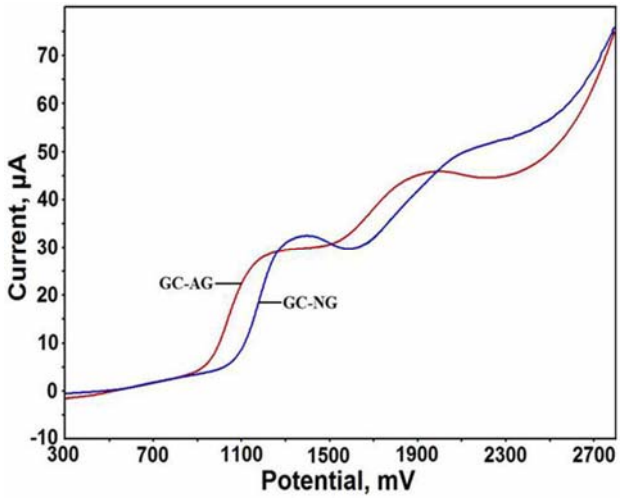


**Fig. 2.** First scan (anodic scan) cyclic voltammograms of AG and NG in MeCN containing 0.1 M TBATFB and 1 mM flavonoid on GC electrode. Scan rate is 0.1 $Vs^{-1}$ and vs. $Ag/Ag^{+}$ (10 mM)

From Fig.2 it is very obvious that the voltammogram profiles are different for the two kinds of flavonoids in MeCN. This shows that the electrochemical oxidation of flavonoids is strongly related to the structure, especially to the number and position of the -OH groups. Since there is no systematic study on the electrochemical oxidation mechanism of flavonoids in both aqueous and non-aqueous media, the flavonoids under investigation are purposely chosen considering their structural differences to elucidate their electrochemical oxidation mechanism.

Cyclic voltammograms of 1 mM AG and NG solutions in MeCN containing 0.1 M TBATFB show several oxidation peaks at the GC electrode. Anodic peaks are observed at 1224 and 1967 mV for AG; 1408 and 2132 mV for NG *vs.* $Ag/Ag^+$ electrode. As Fig. 2 shows, the overall cyclic voltammetric profiles of the flavonoids under investigation in MeCN are similar to that of in aqueous media. Our purpose here is not only to investigate the mechanism of oxidation of flavonoids in solution, but also to investigate the mechanism of deposition of flavonoids to the GC electrode surface. Deposition mechanism will be discussed later in mechanism studies section.

Fig. 3(a) and 3(b) shows the multiscan cyclic voltammograms of AG and NG in MeCN containing 0.1 M TBATFB at the GC electrode. The potential was cycled anodically by 10 scans between +0.3 V and +2.8 V. During the first scan, every flavonoid showed a number of oxidation peaks depending on the structure of the compound at the bare GC electrode. The currents of these peaks decreased as the cycle numbers increased and almost became zero in a few subsequent scans. This type of multiscan voltammogram clearly demonstrates that a film immediately forms after the oxidation of flavonoids at the GC electrode on which flavonoid cannot be oxidized. This electrochemical behavior is analogous to the ones obtained in modification of surfaces with various organic compounds [8,9,19,22]. The immediate decrease of the peak current implies that a monolayer is grafted and the electrode surface is passived just after the generation of the oxidation products of the flavonoid. Multilayer formation is also possible, but the disappearance of the voltammogram clearly indicates the existence of at least a monolayer at the surface. From Fig. 3 it is interesting to note that a quasi-reversible surface peak appears and survives from beginning of the second scan for two flavonoid derivatives, especially apparent for AG and NG. This peak can be attributed to the oxidation of surface confined diphenols to quinones in the anodic scan and vice versa in the cathodic scan due to the existence of large amount of residual water in the media when compared to the small surface concentration of the grafted flavonoid [23]. The flavonoid modified surfaces prepared by the anodic oxidation at the GC electrode surfaces are depicted as GC-AG and GC-NG for AG and NG, respectively.

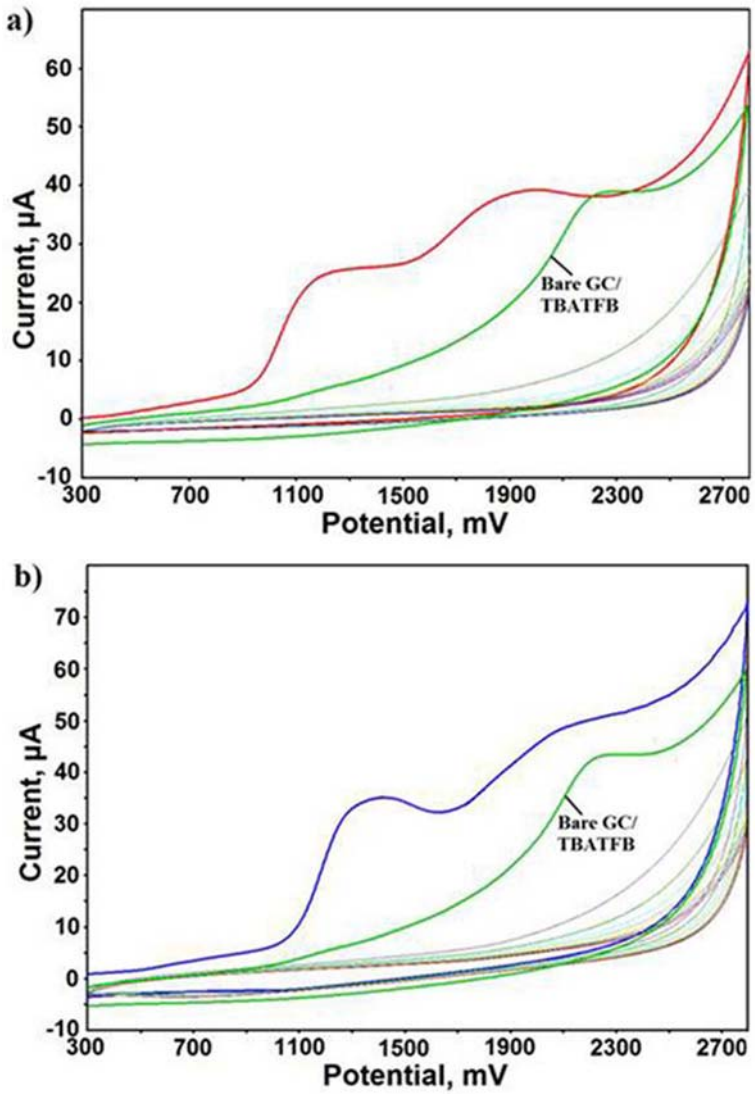


**Fig. 3.** Repetitive cyclic voltammograms of (a) GC-AG and (b) GC-NG in MeCN containing 0.1 M TBATFB and 1 mM flavonoid on GC electrode. Scan rate is 0.1 $Vs^{-1}$ and vs. $Ag/Ag^{+}$ (10 mM) electrode. Grafting was accomplished by 10 sequential scans. Green line voltammogram is for the bare GC electrode in solution without any AG and NG

### 3.2. Characterization of AG and NG modified GC electrode surfaces by CV and EIS

To confirm the existence of flavonoids at the GC electrode surface, cyclic voltammograms of 1 mM ferrocene in MeCN (Fig. 4(a) and Fig. 5(a)) and 1mM hexacyanoferrate-III, ($Fe(CN)_6^{3-}$), at pH 2 in BR buffer (Fig. 4(b) and Fig. 5(b))were acquired on the bare and modified GC. Although the bare GC electrode allows the electron transfer for the ferrocene oxidation, the modified surface does not (Fig.4(a) and Fig. 5(a)).

Fig. 4(b) and Fig. 5(b) shows that the voltammograms of $Fe(CN)_6^{3-}$ in pH 2 of BR buffer solution on the bare GC electrode and after modification of GC electrode with AG and NG.

As it can be seen from Fig. 4(b) and Fig. 5(b), electrochemical response of $Fe(CN)_6^{3-}$ on the flavonoid modified GC electrode has been strongly suppressed by the layers of all kinds of flavonoids. Oxidation-reduction of redox probe species occurs with rapid redox kinetics at the bare electrodes as indicated by the peak shapes of the voltammograms. The inhibition and supression of the rapid electron transfer for this redox system was observed for pH values between 1.81 and 11.98 in BR buffer solution, indicating that electron transfer was not affected by the surface charge density due to the protonation or deprotonation of polyphenol type flavonoids. This behavior may be the evidence of an organic mono layer formed by the two flavonoid derivatives.

The potential scan range is an important parameter in the grafting process of the flavonoids to the GC surface. To investigate the potential scan range, the initial potential was fixed at +0.3 V and the applied potential was changed to the values more positive than the potential of the starting point.

Fig. 4(c) and Fig. 5(c) shows the Nyquist graphs for redox couple of $Fe(CN)_6^{3-/4-}$ solution in 0.1 M KCl at the bare GC electrode and after modification of GC electrode with AG and NG at +0.3 V and +2.8 V potential ranges. Modification begins only when the applied potential is more positive than the last peak potential.

The results of CV and EIS measurements suggest that strongly attached surface films are formed on the GC electrode by imposing anodic scan from +0.3 V to +2.8 V into in MeCN solution containing 1 mM of AG and NG. These films completely block the electrochemical response of $Fe(CN)_6^{3-/4-}$ which shows highly reversible electron transfer rate on the bare GC electrode.

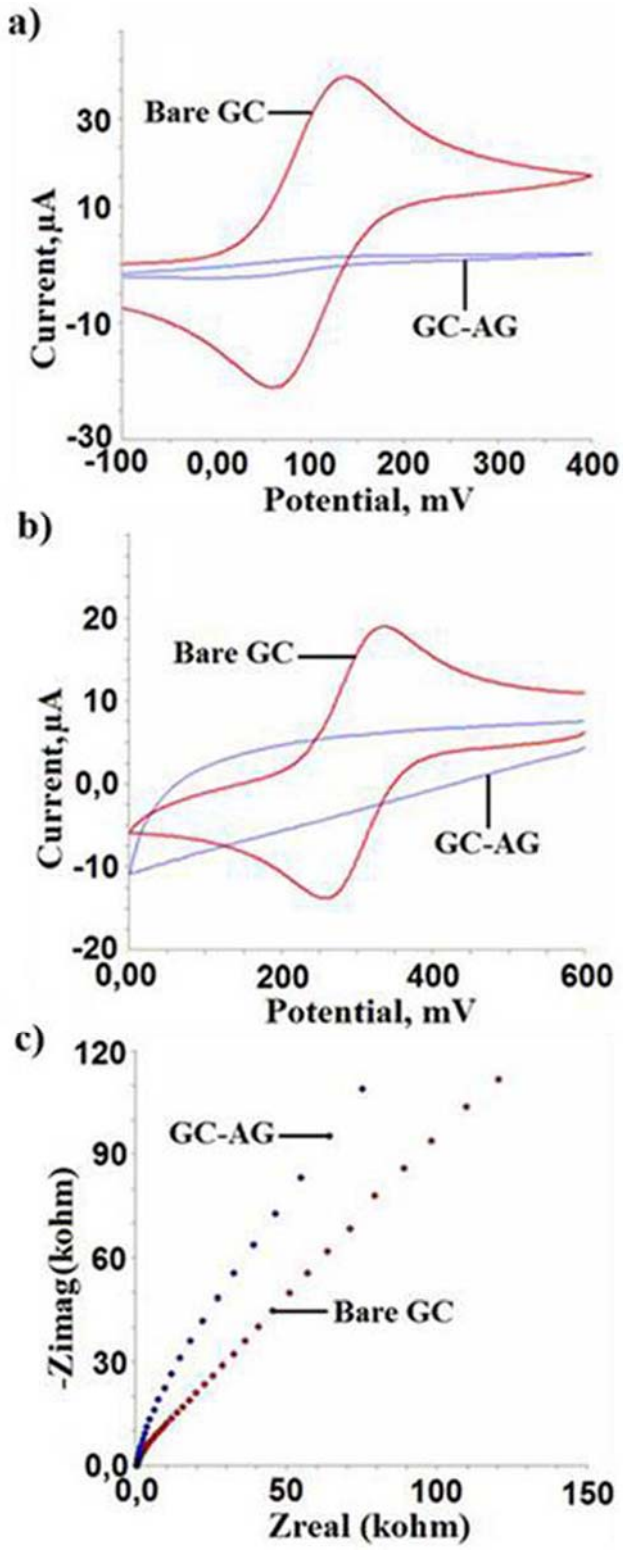


**Fig. 4.** Cyclic voltammograms and electrochemical impedance spectra of GC-AG (a) 1 mM ferrocene *vs.* $Ag/Ag^{+}$ (10 mM) in MeCN + 0.1 M TBATFB, Scan rate is 0.1 $Vs^{-1}$ (b) 1 mM $Fe(CN)_6^{3-}$ *vs.* $Ag/AgCl/KCl_{(sat)}$ in BR buffer solution, pH= 2. Scan rate is 0.1 $Vs^{-1}$ and (c) the redox couple $Fe(CN)_6^{3-/4-}$ solution in 0.1 M KCl at the frequency range of 100.000-0.05 Hz at 10 mV wave amplitude

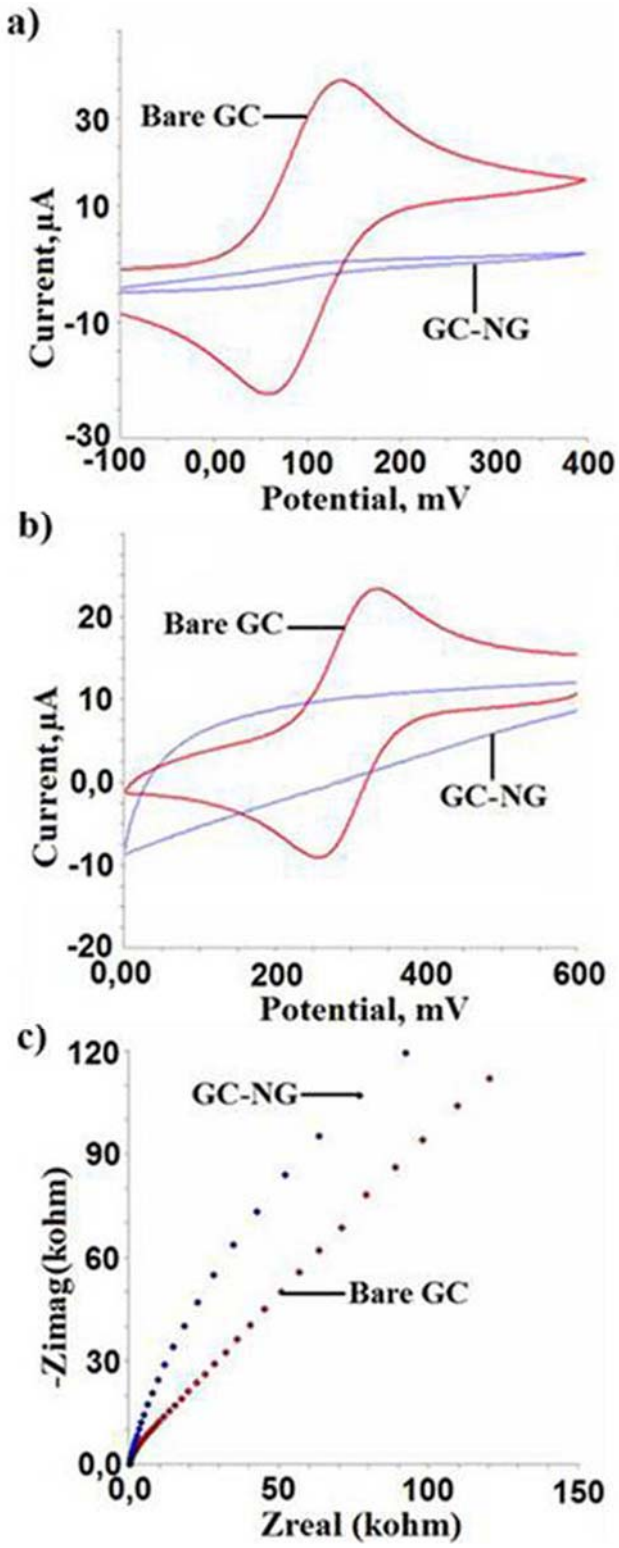


**Fig. 5.** Cyclic voltammograms and electrochemical impedance spectra of GC-NG (a) 1 mM ferrocene *vs.* $Ag/Ag^{+}$ (10 mM) in MeCN +0.1 M TBATFB, Scan rate is 0.1 $Vs^{-1}$ (b) 1 mM $Fe(CN)_6^{3-}$ *vs.* $Ag/AgCl/KCl_{(sat)}$ in BR buffer solution, pH= 2. Scan rate is 0.1 $Vs^{-1}$ and (c) the redox couple $Fe(CN)_6^{3-/4-}$ solution in 0.1 M KCl at the frequency range of 100.000-0.05 Hz at 10 mV wave amplitude

EIS technique was used to investigate the stability of modified surfaces and possible range for the quantification measurements. The measurements were taken in 0.1 M, TBATFB (in MeCN) supported electrolyte between the positive and negative potentials using different potential regions having impedance measurements after each cycle. The results were overlayed and given as Nyquist plot in Fig. 6 and Fig. 7.

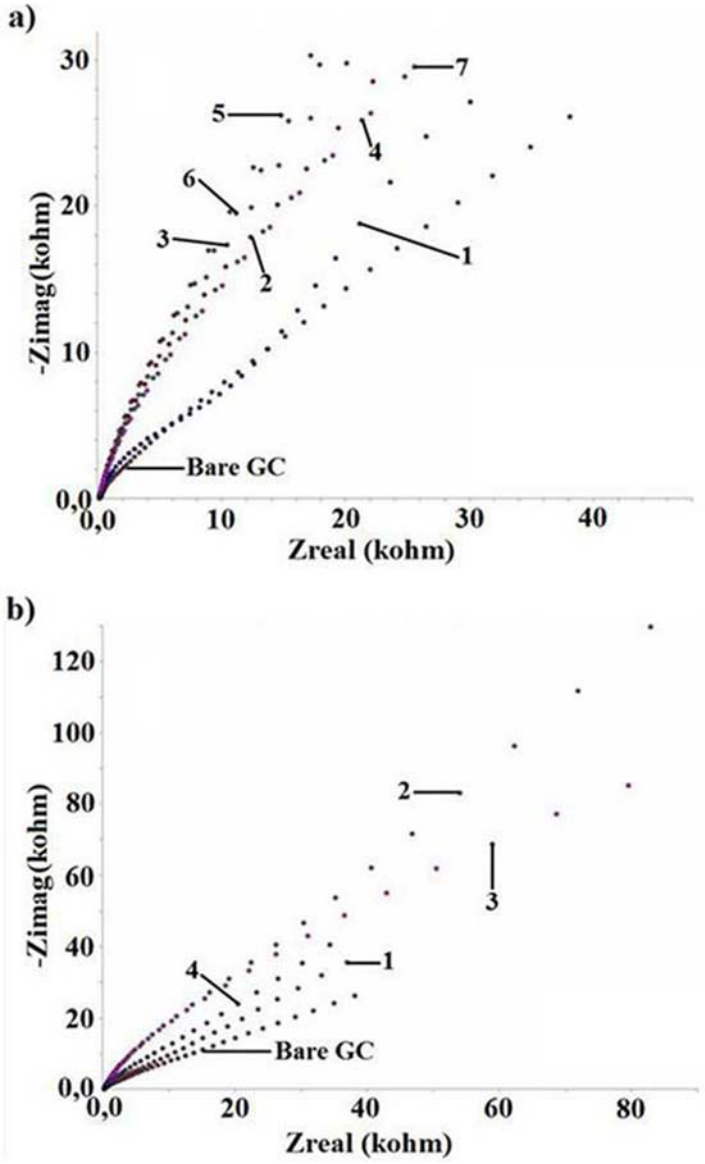


**Fig. 6.** Nyquist curves obtained from the impedance measurements after CV scans of AG modified GC electrode surface in TBATFB supported electrolyte media between various negative and positive potential range **(a)** 0.0/+0.5-0.0/+3.0 V potential range (**1**: GC-AG imp.; **2**: GC-AG, 0.0/+0.5; **3**: GC-AG, 0.0/+1.0; **4**: GC-AG, 0.0/+1.5; **5**: GC-AG, 0.0/+2.0; **6**: GC-AG, 0.0/+2.5; **7**: GC-AG, 0.0/+3.0) **(b)** 0.0/-0.5-0/-1.5 V potential range (**1**: GC-AG imp.; **2**: GC-AG, 0.0/-0.5; **3**: GC-AG, 0.0/-1.0; **4**: GC-AG, 0.0/-1.5), 100000/0.05 Hz

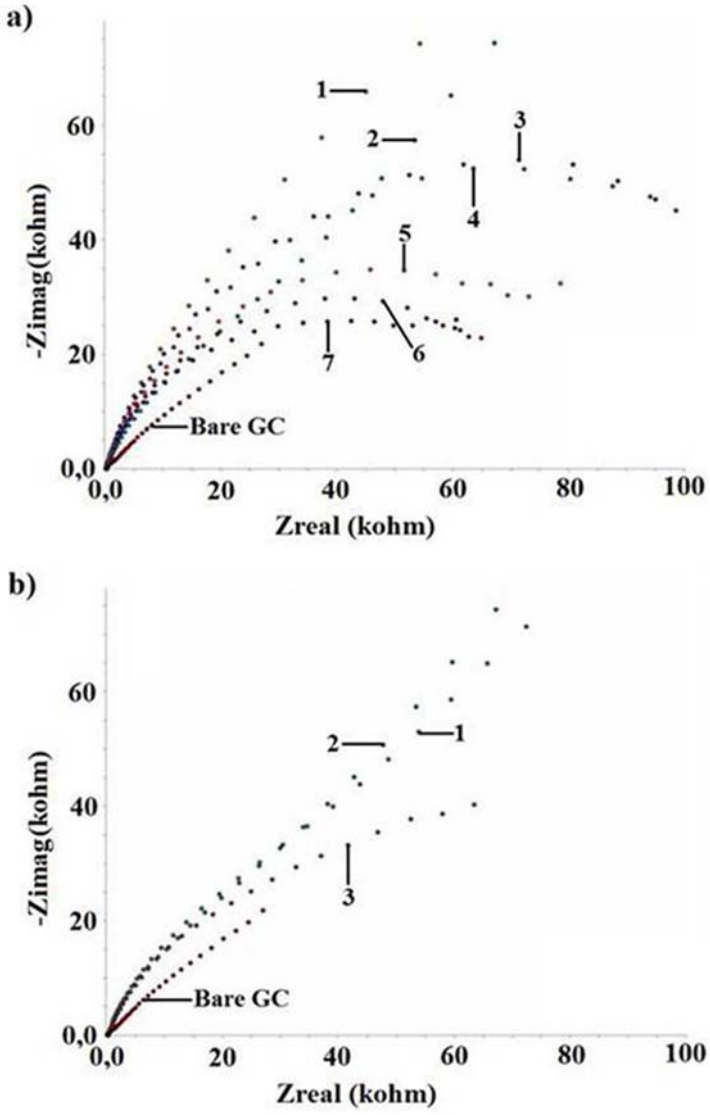


**Fig.7.** Nyquist curves obtained from the impedance measurements after CV scans of AG modified GC electrode surface in TBATFB supported electrolyte media between various negative and positive potential range **(a)** 0.0/+0.5-0.0/+3.0 V potential range (**1**: GC-NG imp.; 2: GC-NG, 0.0/+0.5; **3**: GC-NG, 0.0/+1.0; **4**: GC-NG, 0.0/+1.5; **5**: GC-NG, 0.0/+2.0; **6**: GC-NG, 0.0/+2.5; **7**: GC-NG, 0.0/+3.0) **(b)** 0.0/-0.5-0.0/-1.5 V potential range (**1**: GC-AG imp.; **2**: GC-AG, 0.0/-0.5; **3**: GC-AG, 0.0/-1.0), 100000/0.05 Hz

When the overlay Nyquist curves shown in Fig. 6(a) and 7(a) are examined it can be clearly stated that the two molecules are stable up to +3.0 V. However, the surface stays stable up to -1.5 V for AG (Fig. 6(b) ), and up to -1.0 V for NG (Fig. 7(b) ). Non-destructive impedance test was carried out for the working range. The same test could have been carried out using voltammetric technique with ferrocene, because the surface may be destructed by the applied potential for each time. For this reason, an impedance test having a potential as small as 10 mV was applied to determine working range.

### 3.3. CAM spectroscopic characterization of AG and NG modified GC electrode surfaces

In the CAM technique, if the dropped substance is water, the hydrophilicity of the modified surface can be investigated by comparing the water drop contact angles on both bare GC electrode and flavonoid modified GC electrode. In the current study, bare GC electrode surface was found to be quite hydrophobic, as revealed by a high contact angle of $86^o$, very close to $90^o$. As Table 1 shows, AG molecule bears only one OH group in B ring and two OH groups in A ring, has also a higher contact angle and hence more hydrophilic as compared to NG. Besides, NG molecule bears one OH group in B ring and two OH groups in A ring functional groups, have also a higher contact angle and hence more hydrophobic as compared to AG.

**Table 1.** CAMs of bare and modified GC electrode surfaces corresponding to water

| Surface | Contact angle (º) |
|---|---|
| Bare GC | 86.00 ± 0.50 |
| GC-AG | 39,00 ± 0,27 |
| GC-NG | 41,40 ± 0,30 |

### 3.4. AFM characterization of AG and NG modified GC electrode surfaces

The characterization process revealed the differences between the bare GC electrode and flavonoid modified GC electrode surfaces. All measurements were obtained at the *Tapping mode* for all kinds and a1 μm×1 μm area was scanned. Two dimensional (2D) images of bare GC electrode, GC-AG and GC-NG surfaces were given in Fig.8. This case is the microscopic surface characterized data the proving modification of the surfaces.

### 3.5. Mechanism of the oxidation and the attachment of AG and NG to the GC electrode

Although there are some discrepancies about the oxidation mechanism of flavonoids, almost all researchers agree that the first oxidation occurs in the B ring hydroxyl groups to quinones, either in aqueous or non-aqueous solution [23]. On the other hand, the mechanism of grafting of flavonoids to the solid surfaces is not extensively studied and still responsible of many conflicts. Fig. 9 illustrates the oxidation mechanism of AG and NG in solution and the grafting the quinone products to the oxidized GC electrode surface, in accordance with the voltammograms of these compounds in Fig. 2. All voltammograms display the similar properties with three irreversible oxidation peaks. The first one is for the one-electron oxidation of AG and NG to phenolic radical in B ring [12, 13].

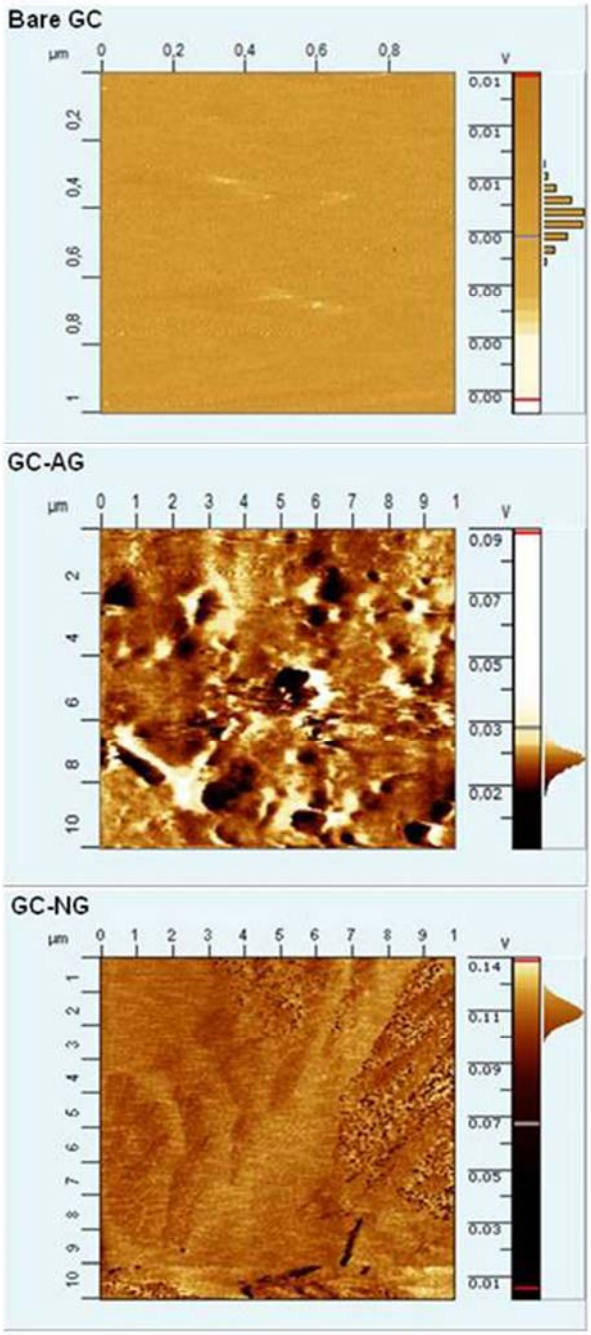


**Fig. 8.** Atomic Force Microscopic 2D images of the bare GC electrode, GC-AG and GC-NG surfaces. Dimensions of the specimen are a 1 μm×1 μm

As stated above, modification occurs only beyond the second peak which is attributed to the oxidation of GC surface with the involvement of residual water in MeCN [23]. As Fig. 9 shows, AG and NG are converted to quinone derivatives with one-electron oxidation of B ring, respectively. Anodically formed quinone derivatives interact with functional groups of the oxidized GC electrode surface beyond about 2 V. Oxygen containing functionalities at the GC surface interact as nucleophiles with quinone rings in positions 6' of AG and NG (B ring)

[23, 24, 25]. Attachment styles of the flavonoids are also depicted in Fig. 9. Deposition of the flavonoid derivatives follows EC (Electrochemical and chemical) mechanism during the electrochemical modification to GC electrode surface forming etheric bonds between flavonoid moieties and GC electrode surface. In summary, every two molecules are electrochemically oxidized to quinones by the application of potential in solution and then these quinone products are chemically bonded to the GC electrode surface through etheric covalent bonds.

It has been concluded that double bond at 2 and 3 position in AG molecule and the single bond between carbon atoms at 2$^{nd}$ and 3$^{rd}$ position in NG molecule are not responsible for the oxidation and binding to the electrode surface, when the mechanism are proposed for the two molecules. Both electrochemical and spectroscopic processes are thought to goes through the ring B which is thought to be the most active site for the two molecules. On the other hand, the double bond between the carbon atom at 2 and 3 positions may be considered as responsible for the oxidation and the binding to the GC electrode surface at lower potential in AG molecule with respect to NG molecule [25].

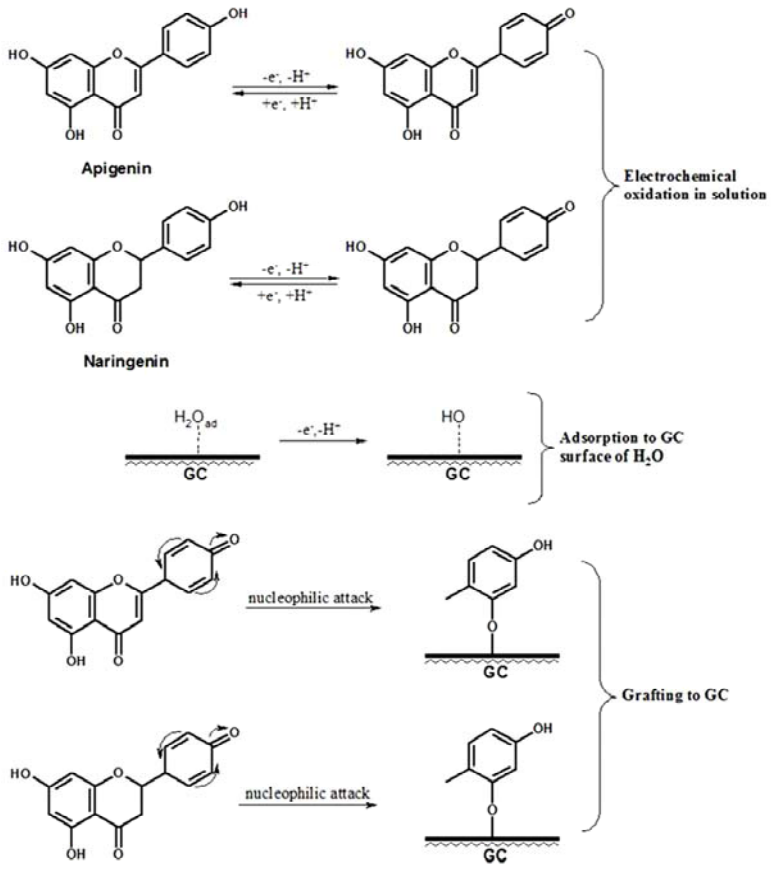


**Fig. 9.** The proposed electrochemical oxidation and grafting mechanism of AG and NG with one-electron process resulting quinone derivative and then grafting to the GC electrode surface

## 4. CONCLUSIONS

Electrochemical modification via the electrochemical oxidation of apigenin and naringenin on the GC electrode in non-aqueous media is reported for the first time. The modification was carried out only in non-aqueous media, while the electrochemical characterization was done in both aqueous and non-aqueous media. We also propose a grafting mechanism of apigenin and naringenin to the GC electrode surface.

**Acnowledgements**

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