Fast growing environmental issues, clinical problems, food control and industrial analysis all seek a useful platform for onsite monitoring. Over the past few decades, several materials were developed for the onsite monitoring of pollutants, biological compounds, food samples and industrial compounds.1 In which, the carbon-based materials dominate the field of sensors. In particular, screen-printed carbon electrodes (SPCEs) have been widely employed for their robustness, cheap price, versatility and availability.2 However, as-prepared SPCEs are electrochemically inert because the SPCEs are prepared from pyrolytic carbon and certain polymer inks. Usually, the carbon is mixed with the graphite and a variety of binders (viz., acrylics, alkyls, vinyls, epoxies, polyurethane resins or phenolic resins) then printed on the substrate of interest. Herein, the binder is selected by the choice of substrate, film flexibility curing temperature, and the resin compatibility. Therefore, this binder makes the charge transfer resistance high at the electrode-electrolyte interface, which slow down the electron transfer kinetics and results in quasi-reversible or irreversible redox processes.3 To resolve these issues, an SPCE was subjected to pretreatment with mechanical, electrochemical, chemical, radiofrequency plasma and thermal techniques. Interestingly, the pretreated SPCE shows a dramatically improved electron transfer rate and voltammetric peak shape. Therefore, the pretreatment of SPCEs has generated substantial interest from researchers.1,4

Recently, several varieties of electrochemical pre-anodization procedures were developed to activate SPCEs. In particular, Compton’s and Zen’s groups studied the electrochemical pre-anodization of SPCEs and characterized the edge plane and basal plane effects. Their studies suggested that the edge plane of pre-anodized SPCEs show better electrocatalytic activity than the basal planes.5 However, SPCEs consist of pyrolytic graphite that contains both edge planes and basal planes with a ratio that depends on the quality of the pyrolytic graphite.6 Moreover, Zen’s group studied the electrochemical behavior of pre-anodized SPCE with biological compounds such as ascorbic acid (AA), dopamine (DA) and uric acid (UA). They demonstrated the influence of the oxygen moieties in the active edge sites of SPCEs toward the simultaneous determination of AA, DA and UA.7 Additionally, they investigated the electrochemical determination of creatinine and NADH by a pre-anodized SPCE.8,9 In contrast, Compton’s group demonstrated the edge plane effect of SPCEs toward the simultaneous determination of DA, serotonin and AA.10 Additionally, some other researchers studied the simultaneous determination of HQ and CC on the pretreated SPCE.11 Previous reports have documented the superior electrocatalytic activity of pretreated SPCEs with various biological compounds. These studies motivated us to evaluate the selectivity of pretreated SPCEs toward identical structural compounds. Thereby, we selected the catechol-containing compounds, i.e., CC, CA and DA. Additionally, we choose HQ because it has a similar oxidation potential to the catecholic functional groups.

In general, DA is an essential biological compound that acts as a neurotransmitter, which makes of great interest for clinical analysis.12 CA is an anti-oxidant present in red wines and some natural products that has received interest because it is in human diets.13 Finally, HQ and CC are environmental pollutants discharged from industrial plants.14 These all have unique functions or harmful effects, thus, the determination of these molecules is an important task. Several methods have been developed to detect these molecules, but the electrochemical method provides an effective and low cost means.15–18 Therefore, in this work, the above mentioned molecules are electrochemically determined by the pretreated SPCE and compared its electrochemical activity with other pretreated carbonaceous materials including carbon nanotubes (CNTs), graphene oxide (GO) and graphite (GR). Interestingly, the higher electrochemical activity was observed from the pre-anodized SPCE (aSPCE) and activated GR (aGR) than the functionalized CNT (f-CNT) and reduced GO (rGO), because, the aSPCE and aGR have large number of active edge planes than that of f-CNT and rGO. However, the edge plane active sites are even higher at aSPCE than the aGR, therefore, the pretreated SPCE exhibited higher electrocatalytic activity compared to the other carbon materials.15–18 Moreover, selectivity is the major drawbacks in electrochemical method.

Hence, in the present work, we concentrate on investigating the effect of interference on the determination of catecholic functional groups. Briefly, DA and CC are derived from catechols (dihydroxybenzene) that are oxidized between 0.18 to 0.23 V depending on the carbon electrode matrix. We have independently investigated the electrochemical performance of these molecules on an untreated SPCE and a pretreated SPCE. The behavior of the pretreated SPCE exhibited a drastic change and showed better sensitivity. Then, the selectivity was determined by a table analysis where one molecule was kept constant and the other three molecules were varied. Finally, the interference signals were investigated and tabulated to better understand these phenomena.
Materials and Methods

Materials.—Catechol (CC), dopamine (DA), caffeic acid (CA), hydroquinone (HQ), glucose, ascorbic acid (AA), uric acid (UA), disodium hydrogen phosphate (Na2HPO4), sodium dihydrogen phosphate (NaH2PO4) and all the other chemicals were purchased from Sigma-Aldrich chemical Co., Alfa-Aesar and Fluka chemicals. All of the reagents were of analytical grade and were used as received. The screen-printed carbon electrode (SPCE; working area = 0.07 cm2) were purchased from Zensor R&D Co., LTD., Taiwan.

Methods.—The pre-anodized surface was probed using scanning electron microscopy (SEM Hitachi S-3000 H) and the edge planes were investigated using a Raman spectrometer (Dong Woo 500i, Korea) equipped with a charge-coupled detector. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using a CHI 405a and CHI 900 electrochemical workstation, respectively. All the electrochemical studies were conducted in a conventional three electrode system using a SPCE or an aSPCE as a working electrode (area 0.07 cm2), platinum wire as a counter electrode and saturated Ag/AgCl (saturated KCl) as a reference electrode. A 0.05 M phosphate buffer (PB) solution (pH 7) was used for all the electrochemical experiments.

Pre-treatment of the SPCE.—Prior to the experiments, the SPCE was pre-cleaned with ethanol and water. Then, the SPCEs were activated by CV in a 0.05 M PB (pH 5) solution in a potential window of −0.5 to 2 V for 10 cycles with the scan rate of 50 mV/s. After the activation, the SPCEs were gently rinsed with water and dried at room temperature. The activated SPCEs (aSPCEs) were directly applied to the electrochemical studies.

Preparation of other materials.—The f-CNT, rGO and aGR were used to compare the performance of the aSPCE. Herein, the CNT was functionalized by the KOH activation process, thereby, 5 mg of CNT were dispersed in 10 mL of 1 M KOH solution and sonicated for 3 hours. Furthermore, the KOH activated CNT was used to compare the performance of the aSPCE. Herein, the CNT was functionalized by the KOH activation process, thereby, 5 mg of CNT were dispersed in 10 mL of 1 M KOH solution and sonicated for 3 hours. Functionalization of the CNT was achieved by treatment with 25 wt% KOH solution. After sonication, the CNT was washed with water and dried at room temperature.

Characterization.—To confirm the pre-anodization process, the aSPCE was investigated using Raman spectroscopy, which is a unique technique for evaluating the defects and disorder in carbon materials. Thus, Raman spectroscopy was used to investigate the disorder in the SPCE and the aSPCE. The f-CNT, rGO and aGR were used to compare the performance of the aSPCE. The peaks appearing at 1360 and 1603 cm−1 were attributed to the D (disordered) band and the G (graphitic) band, respectively. The D band corresponds to the disruption of the sp2 carbon symmetry, which commonly considered the basal plane. Furthermore, the effect of the pre-anodization process on the local surface was probed using SEM. Significant changes were identified from the SEM images of the SPCE and the aSPCE (Figs. 1b and 1c). As mentioned above, the SPCE consists of pyrolytic graphitic carbon which exhibits a flake-like morphology. After the pre-anodization process, the SPCE was revealed to have a corroded surface. Moreover, as shown in Fig. 1d, the edges of the graphitic flakes were highly pitted. This result suggested that the pre-anodization process introduced edge planes and altered the surface morphology of the SPCE.

Electrochemistry of SPCE and other carbon materials.—The electrochemical active surface areas (A_surface) and heterogeneous rate constants (k_{eff}) of the aSPCE, f-CNT, rGO and aGR were investigated from the surface sensitive inner sphere ferricyanide ([Fe(CN)6]3−/4−) redox probe. Fig. S1 shows the CVs of aSPCE, f-CNT, rGO and aGR which are carried out in 0.1 M KCl containing 5 mM [Fe(CN)6]3−/4−. It can be seen that the well-defined redox behavior for all the electrodes corresponds to the redox reaction of [Fe(CN)6]3−/4−. However, the aSPCE shows lower redox peak current than the other carbon electrodes. Therefore, it is less surface sensitive to the other carbon materials. As a result, the A_surface and the k_{eff} of aSPCE are lower than the other carbon materials. The A_surface was investigated by the Randles-Sevck equation by utilizing scan rate studies in [Fe(CN)6]3−/4− from 0.01 to 0.2 V/s (Fig. S2). The Randles-Sevck equation as follows:

\[
i_p = 2.69 \times 10^5 n^{3/2} A^{1/2} D^{1/2} V^{1/2}
\]

Where \(i_p\) is anodic or cathodic peak current, \(A\) is a diffusion coefficient of [Fe(CN)6]3−/4− (7.6 × 10−9 cm2 s−1), \(C\) is concentration of the [Fe(CN)6]3−/4− (mol cm−3), \(A\) is electroactive area (cm2), \(n\) is number of transferred electrons and \(V^{1/2}\) is square root of scan rate (V s−1). From the results, the calculated A_surface are 0.130, 0.302, 0.137, and 0.166 cm2 for the aSPCE, f-CNT, rGO and aGR, respectively. Herein, the surface sensitivity to the redox probe of various carbon materials following the order of aSPCE < rGO < aGR < f-CNT. Moreover, the k_{eff} of aSPCE, f-CNT, rGO and aGR was calculated by the following equation:

\[
\Psi = k_{eff}^{3/4} \pi D n F / R T^{1/4}
\]

Where \(\Psi\) is a kinetic parameter, \(R\) is a gas constant, \(F\) is a Faraday constant, \(D\) is a diffusion coefficient of [Fe(CN)6]3−/4− (7.6 × 10−9 cm2 s−1), \(C\) is concentration of the [Fe(CN)6]3−/4− (mol cm−3), \(n\) is number of transferred electrons participated in redox process, and \(T\) is temperature (K). The \(\Psi\) is tabulated as a function of \(\Delta E_p\) (peak-to-peak separation) at a temperature (298 K) for a one electron process (where the charge transfer coefficient, \(a = 0.5\)). The kinetic parameter was calculated as a function of \(\Delta E_p\) by using the Nicholson method. The empirical equation as follows:

\[
\Psi = (−0.6288 + 0.00214X) / (1 − 0.017X)
\]

Where X = \(\Delta E_p\) in mV used to determine the \(\Psi\) as a function of \(\Delta E_p\), which are obtained from the experiments of CV at various scan rates. This CV experiment was conducted in [Fe(CN)6]3−/4− for scan rates 52.11.211.149 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Figure 1. Raman spectra of SPCE and aSPCE (a). SEM image of SPCE (b) and low magnification (c) and high magnification (d) SEM images of aSPCE. XPS high resolution C 1s core level spectra of SPCE (e) and aSPCE (f).

from 0.01 to 0.2 V/s, and the ΔE_p is ranging from 98–164 mV. Later, the Ψ was plotted against the [πDνF/RT]^{-1/2}, from the slope we can calculate the k_{eff}.27,28 The obtained k_{eff} values are 6.91 × 10^{-4}, 7.83 × 10^{-4}, 7.44 × 10^{-4} and 7.147 × 10^{-4} cm s^{-1} for the aSPCE, f-CNT, rGO and aGR, respectively.

Electrocatalysis of aSPCE and other carbon materials toward catecholic derivatives.—As discussed above, the aSPCE revealed lower performances in terms of surface area and rate constants than the other carbon materials. Mostly, the ferricyanide redox probe was utilized to investigate the surface properties of materials of interest. However, we realize that the aSPCE have different electrochemical activity when it reaches to catecholic compounds. Fig. 2 compares the electrochemical behaviors of 100 μM HQ (a), CC (b), CA (c) and DA (d) on the SPCE and aSPCE in 0.05 M PB (pH 7) solution at a scan rate of 50 mV/s. Interestingly, remarkable variations are found among all of the compounds in the reaction rates with aSPCE. For instance, a considerable decrease in the peak to peak separation (ΔE_p) was observed at aSPCE such as 92, 81, 58 and 31 mV for HQ, CC, CA and DA, respectively whereas the SPCE revealed 480, 364, 275 and 285 mV for the HQ, CC, CA and DA. Moreover, the oxidation peak current of each of these four compounds with the aSPCE are higher.
than that with the SPCE. Additionally, compared to those with the SPCE, the oxidation peak potential of each of these four compounds was substantially lowered when using the aSPCE, which showed oxidation potential onsets at 0.055, 0.133, 0.142 and 0.112 V for the HQ, CC, CA and DA, respectively. Among the four compounds, DA shows the highest oxidation peak current due to the highly oriented edge active sites of aSPCE and also the amine group makes the DA positively charged at pH 7 so it adsorbs to the electrode at the start of the scan (−0.2 V). Herein, CC, CA and DA have catechol functional groups, which oxidized to form ortho-quinone derivatives by a two-electron transfer process.12–14 However, all four molecules are highly active with the aSPCE when compared with the SPCE and are responsive to electrochemical determination. It is due to the occurrence of large number of edge plane active sites on aSPCE surface. Incidentally, the pretreated form of other carbon materials doesn’t reveal a good electrocatalysis like aSPCE, however, it revealed better activity when compared to non-pretreated carbon materials. It can be seen from Figs. 2e–2h, CV curves of CNT and f-CNT in the HQ, CC, CA and DA exhibited the drastic variations. The f-CNT revealed high background current which attributed to the specific adsorption of electrolyte ions in its interface (double layer capacitance). Unlike the 2D carbons, the CNT poses different basal and edge plane activities that are mainly corresponds to the double layer capacitance. Mainly, the CNT possess maximum basal plane with minimum edges. Hence, during the functionalization, carboxylic functional groups are initially formed on basal planes, later it will convert to other functional groups. From Figs. 2e–2h, we can identify the carboxylic acid functional group in CNT by the oxidation peak at ∼0.62 V. This –COOH group is helps to capture the Na+ from the electrolyte as –COONa. Therefore, the high background current overwhelmed the electro-oxidation of catecholic compounds. Similarly, the rGO also exhibited maximum highly disordered basal plane (surface defects) and minimum edge active sites, which also produce more capacitance Figs. 2i–2l. But, this phenomenon was different in the case of GR and aGR. The rationale behind this different activity was depends on their basal plane and edge plane activity. Although, unlike the GO and CNT, the GR is having relatively different structural properties. It has more edge planes because of its layered arrangement. Therefore, the non-pretreated GR exhibited the better electrocatalytic activity to the catecholic compounds when compared with aGR (in terms of peak shape), because, during the activation the layered graphite sheets were exfoliated into bunch of few layers of graphite oxide. As a result, the graphite sheets meet high disorder and also the more oxygen functionalities on the basal plane forces the aGR into more capacitance Figs. 2m–2p. As said above, all three carbons (f-CNT, rGO and aGR) exhibited the high background current, most of the generated active sites (during pretreatment) are involved in double
layer capacitance. It can be concluded that, the pretreatment process produces the active sites at the basal planes of the carbon materials which directly undergoes the charge-discharge properties. Therefore, the minimum of edge active sites only participated in the electrocatalysis of catecholic compounds. To confirm the reaction process, the scan rate study was performed for each analyte with different carbon materials.

Effect of scan rate.—Fig. 3 shows the CVs of 100 μM HQ (a), CC (b), CA (c) and DA (d) on the aSPCE in 0.05 M PB (pH 7) solution at various scan rates ranging from 10 to 200 mV/s. The redox peak current of these four molecules increased while the scan rate increased because higher scan rates cause the diffusion layer to become very thin, allowing more of the active species to form from the bulk. Thus, the flux near the electrode surface is higher at higher scan rates, which increases the current, as it is directly proportional to the flux. However, the anodic and cathodic peak potentials were slightly shifted to positive and negative directions, respectively, when increasing the scan rates for DA (d). This result indicated that the oxidation of DA with the aSPCE is a quasi-reversible process. The anodic peak currents of HQ (a), CC (b), and CA (c) were plotted against the square root of the scan rate and DA (d) was plotted against the scan rate. Fig. 3 (inset) shows linear fits for the plots of all the four molecules where HQ (a), CC (b) and CA (c) appear to be diffusion-controlled and DA (d) follows an adsorption-controlled process. However, these four molecules at f-CNT and rGO exhibited the adsorption-controlled process Figs. 4 and 5, because of highly exposed basal planes. This phenomenon was well supported with the previous discussions and further confirmed the slow kinetics of those four molecules. In particular, the scan rate studies of those four molecules at rGO revealed a poor electro-oxidation. Therefore, f-CNT and rGO are more surface sensitive and also the high background signal is inevitably interfering with the sensitivity of the sensor response. On the other hand, the aGR exhibited acceptable oxidation responses with those four molecules wherein it revealed the adsorption-controlled reaction for CA and DA; and diffusion-controlled reaction for HQ and CC (Fig. 6). In contrast, the aSPCE and aGR showed the better performance with those four molecules than that of f-CNT and rGO. However, the electrode modification and activation process of the aGR is quite complex, moreover, the electrode prone to the fouling effect. Therefore, this investigation has provided insight into the type of reaction that these four molecules undergo on various carbon materials. And also, this study is allowing us to investigate the sensitivity of the electrochemical determination of these four molecules at aSPCE.

Sensitivity of HQ, CC, CA and DA to the aSPCE.—Fig. 7 shows the DPVs of various concentrations of HQ (a), CC (b), CA (c) and DA (d) on the aSPCE in a 0.05 M PB solution. The peak oxidation currents increased as the concentration of (a) HQ was increased from 0.3 to 930 μM, (b) CC was increased from 0.05 to 1972 μM,
Figure 4. CVs responses of f-CNT in the presence of 100 μM HQ (a), CC (b), CA (c) and DA (d) for various scan rates ranging from 10 to 200 mV/s. The inset shows the corresponding linear fits for the plots of oxidation peak vs. scan rate for HQ (a), CC (b), CA (c) and DA (d).

(c) CA was increased from 0.05 to 1350 μM and (d) DA was increased from 0.03 to 100 μM. The peak oxidation current of the HQ (a), CC (b), CA (c) and DA (d) was plotted against the concentration of each analytes, respectively. As shown in Fig. 7 (inset), the linear concentration range and sensitivity were calculated to be 0.3–930 μM, 0.05–1367 μM, 0.03–50 μM, and 0.03–0.01 μM, 0.22 μM and 1.516 μA μM⁻¹ cm⁻² for HQ, CC, CA and DA, respectively. The lowest limit of detections (LOD) of HQ, CC, CA and DA were calculated by the modern IUPAC recommendation based on type I error (false positive possibility: mostly <1%) and type II error (false negative possibility ~50%). The LOD was calculated to be 0.103, 0.031, 0.042 and 0.011 μM for HQ, CC, CA and DA, respectively. From all of the calibration plots, it can be noted that low concentrations of the analytes exhibited higher sensitivities, causing them to fit different linear calibration functions at low concentrations. Thus, all the determinations with the aSPCE follow two linear calibration ranges; however, we have merged them and given them as one linear range. The obtained analytical parameters are comparable with those for previously reported carbon-based sensor electrodes. Therefore, these results were compared with previously published results, as tabulated in Tables S4-6. However, the major problem of this determination method is its selectivity because all four of these molecules are oxidized at somewhat similar potentials. Hence, there may be a selectivity problem among these four molecules. We have carefully analyzed the selectivity of these molecules and discuss our findings below.

Interference study.—As mentioned and discussed above, the aSPCE could effectively determine HQ, CC, CA and DA compared with the SPCE. This detailed study showed that the aSPCE possesses appreciable sensitivity, stability and acceptable reproducibility. However, selectivity is a noteworthy factor when applying the aSPCE in real time sensing. Hence, in this study, we have investigated the selectivity among similarly structured compounds, i.e., HQ, CC, CA and DA, in a 0.05 M PB (pH 7) solution. Of the four molecules discussed herein, three possess an electrochemically active catechol group. In all the interference experiments, one analyte was kept constant and the concentrations of the other three molecules were varied (with 100 μM as the optimized concentration). Fig. 8a shows the DPVs of HQ in the presence of CC, CA and DA, wherein the oxidation of HQ is not affected by the other three molecules because, when compared with CC, CA and DA, HQ possess different oxygen functionalities. Therefore, HQ shows a distinct DPV waveform in the presence of CC and CA. However, its oxidation peak did merge with that of DA. As mentioned above, the DA exhibited a high electrocatalytic activity with the aSPCE, and thus it diminished the DPV waveform of HQ. This behavior can be clearly seen in Fig. 8d, where the response of HQ was dominated by that of DA. In contrast, the oxidation of CC and CA does not affect the DPV signal of HQ (Figs. 8b and 8c), allowing us to conclude that the oxidation of HQ is not influenced by catechols (CC, CA and DA). Likewise, CC, CA and DA were investigated in the presence of the other molecules. The peak oxidation currents of CC and CA are not drastically altered, unlike DA, whose peak current does change...
Figure 5. CVs responses of rGO in the presence of 100 μM HQ (a), CC (b), CA (c) and DA (d) for various scan rates ranging from 10 to 200 mV/s. The inset shows the corresponding linear fits for the plots of oxidation peak vs. the scan rate for HQ (a), CC (b), CA (c) and DA (d).

for the same reason discussed above. Thus, this study confirmed that quinone groups approach the aSPCE in a different orientation. Until now, we have concentrated on the catecholic functionalities of CC, CA and DA. Figs. 8b and 8c displays the DPV signals for the CC and CA, which exhibited a drastic current change after the addition of DA, revealing a considerable interference with CA and CC. This study shows that the catecholic functionalities interfere strongly with each other, but the secondary functional groups on the aromatic ring significantly alter their electrocatalytic activities. Additionally, the superior performance of DA is also affected by CC and CA, which suppressed the electrocatalytic activity of DA by 15 and 23%, respectively (Fig. 8d). To better understand these interference signals, they were tabulated in Table S7. Here, the actual peak oxidation current was fixed at 100% and the relative interference signal was calculated using the DPV data. From Table S7, we can clearly see that DA influenced the overall electrocatalytic activity and interfered with other molecules, changing their signals drastically. This study concluded that the aSPCE cannot distinguish among the catecholic functionalities because the DPV wave forms are overlapped for all three of the molecules (CC, CA and DA). Therefore, individual determinations of these molecules are possible, but some limitations too exist. The results from throughout this study show that the simultaneous determination of HQ and CC with the aSPCE is possible because it is highly selective for each and continues to detect in the presence of common interferences. Therefore, we have performed the simultaneous determination of HQ and CC in 0.05 M PB solution at various concentrations ranging from 20 to 100 μM (Fig. S3). The peak oxidation currents of HQ and CC were increased while the concentrations increased. This study suggested that the simultaneous determination of HQ and CC is possible with aSPCE.

Stability, repeatability and reproducibility.—The stability, repeatability and reproducibility of the aSPCE in detecting HQ, CC, CA and DA were investigated by DPV. DPV was performed for the oxidation of 100 μM HQ, CC, CA and DA in a 0.05 M PB solution for 20 consecutive measurements. There was little variation from the initial oxidation currents of HQ, CC, CA and DA after 20 measurements; they retained 94.1, 96.3, 95.2 and 91.8% of their initial performance with RSD of 1.78, 1.82, 1.91 and 2.44%, respectively. Additionally, the storage stability of the aSPCE sensor was monitored using DPV for the determination of HQ, CC, CA and DA for consecutive weeks. Lasting six consecutive weeks, the study showed that the aSPCE was stable, retaining 98.4, 97.8, 98.1 and 98.2% of the oxidation currents for HQ, CC, CA and DA, respectively. This result confirmed that the aSPCE has good operational stability, repeatability and storage stability. The reproducibility of the aSPCE was scrutinized in a 0.05 M PB (pH 7) solution containing 100 μM of HQ, CC, CA and DA using DPV. Ten individual experiments were performed for HQ, CC, CA and DA, which revealed that all the different electrodes had similar responses with RSD of 2.44, 2.51, 2.43 and 2.82%, respectively.
Figure 6. CV responses of aGR in the presence of 100 μM HQ (a), CC (b), CA (c) and DA (d) for various scan rates ranging from 10 to 200 mV/s. The inset shows the corresponding linear fits for the plots of oxidation peak vs. the square root of the scan rate for HQ (a), CC (b), and shows the linear plot of peak current vs. scan rate for CA (c) and DA (d).

Figure 7. DPV signals of aSPCE in various concentrations of HQ (0.3 to 930 μM) (a), CC (0.05 to 1972 μM) (b), CA (0.05 to 1350 μM) (c) and DA (0.03 to 100 μM) (d). The inset shows the corresponding calibration plot for HQ (a), CC (b), CA (c) and DA (d).
Figure 8. Interference signals of HQ in the presence of CC, CA and DA (a), CC in the presence of HQ, CA and DA (b), CA in the presence of HQ, CC and DA (c) and DA in the presence of HQ, CC, CA (d). All experiments were conducted using DPV and an optimized concentration of 100 μM for the interference experiments.

Conclusions

We have demonstrated the feasibility of using a pretreated SPCE for the determination of HQ, CC, CA and DA. In contrast, with the SPCE, the aSPCE revealed a very low overpotential and a low peak-to-peak separation for the electrochemical activity of HQ, CC, CA and DA. Further, the edge plane activity of various carbonaceous materials was investigated and reported. This report paves the knowledge of edge plane and basal plane activity toward the catecholic compounds. From the detailed study, we have concluded that the similar catechol functional groups of CC, CA and DA are highly interfering with each other. However, the quinone functional group does not interfere with the aforementioned compounds. Hence, the simultaneous determination of HQ and CC is possible using an aSPCE. Moreover, we have demonstrated the individual determinations of HQ, CC, CA and DA on an aSPCE, which exhibited acceptable sensitivity and reproducibility. Therefore, this report details the interference of the catecholic functional groups and will promote further research on pretreated, pyrolytic graphite electrodes.

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