RSC Advances

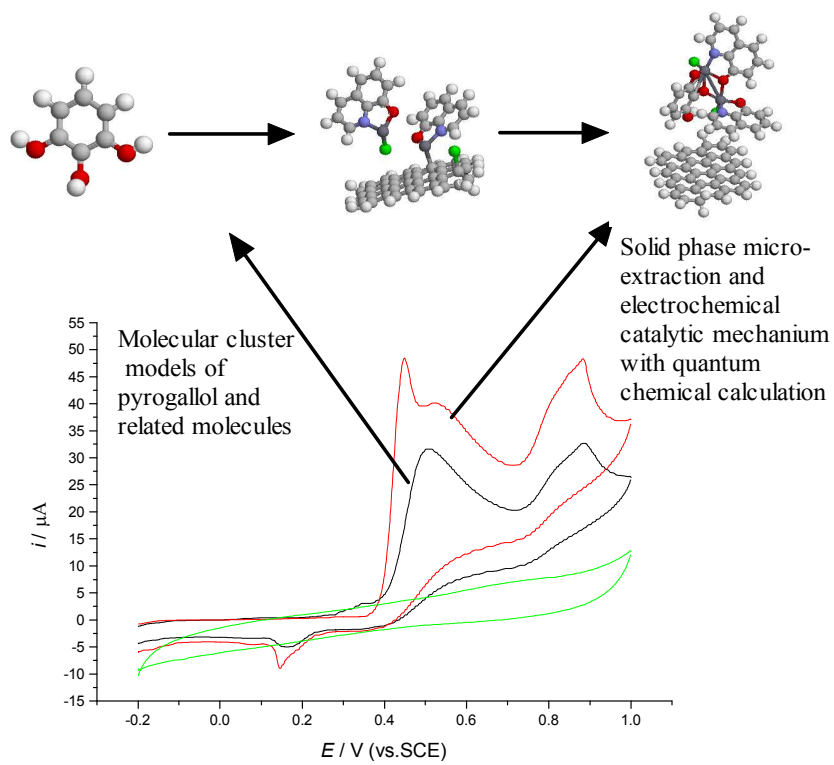# Quantum chemical study on electrochemical behaviorand solid phase microextraction of pyrogallol at Aluminu-8-hydroxylquinonoline modified carbon paste electrode

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Graphic Abstract

Molecular cluster models of pyrogallol and related molecules

Solid phase micro-extraction and electrochemical catalytic mechanium with quantum chemical calculation

ARTICLE TYPE

Quantum chemical study on electrochemical behaviorand solid phase microextraction of pyrogallol at Aluminu-8-hydroxylquinonoline modified carbon paste electrode

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Quantum chemistry calculation was performed with PM6 in MOPAC2012 software based on the molecular cluster models of a piece of graphene including 38 carbon atoms as the surface of graphite
10 powder, and 8-hydroxylquinoline-alumium complexes and pyrogallol in vacuum conditions. The calculation results show that all the molecular cluster models are thermodynamic stable with negative reaction free energy changes. The frontier orbital analysis give out an electron transfer induced electrochemical catalytic mechanism. The descriptor of exchangeable electron well describes the catalytic behavior of pyrogallol at the modified CPE with 55.7% of oxidation peak current and linear relationship
15 between calculated frontier orbital energies and oxidation peak potentials.

Introduction

Pyrogallol among the polyphenols is a very important chemical reagent to be used in detection of peroxidase activity with
20 autooxidation behavior, and has been deeply studied by several methods.[1-4] The microextrations and electrochemical catalytic oxidation of pyrogallol on the 8-hydroxy-quinoline aluminum complex modified carbon paste electrode has been investigated previously in our group.[5] The results shown the electrochemical
25 catalytic oxidation increase oxidation peak current about 53% and a negative shift of oxidation potential about 59 mV, and solid phase microextraction from 8-hydroxyquinoline-aluminum modifier together with a liquid phase microextraction from methyl silicone oil follows a second order adsorption mechanism
30 compared between modified and unmodified CPEs. Now, we try to find some more directive evidences to support these electro-catalytic phenomena as well as from references. Quantum chemical methods have been developed to a new era, and have been applied in many systems in chemistry,[6] environmental and
35 biochemical systems.[7] Quantum chemical methods in dealing with electrochemical problems have a long history, a successful example was dealing with electron transfer rate by Professor Marcus.[8] Carbon paste electrode (CPE) being composed of graphite powder as solid phase and organic solvent as binder has
40 been widely used in all areas in electrochemistry,[9-11] but the Theoretical or quantum chemical studies on CPE has very few reports [12,13] in literature due to the difficulty to model graphite

powder. In this paper, the graphite powder surface was modeled as a piece of graphene with 38 carbons, and whole working
45 electrodes were modeled as molecular clusters composed of the graphene, modifier and the target molecules. The semi-empirical molecular orbital method was performed with PM6 program in mopac2012 software package,[14,15] and the calculated results were analyzed in thermodynamic and frontier orbital theoretical
50 concepts. Some interesting results were reported here.

Molecular models and calculation details

molecular cluster models

Graphite powder may be considered as a stratification of multiple grapheme sheets. The molecular cluster model of graphite
55 powder surface in quantum chemical studies can be approximately described as a pieces of graphene sheet, a part of a layer in a graphite exposed to the surface of graphite powder.[12,13] In this study, the graphene sheet was composed of 38 carbon atoms in match-join form of twelve six-carbon rings, and labeled
60 as C38 in figure 1. Molecule of pyrogallol in **Fig.1** was labeled as Py. The graphene sheet is modified by one Aluminum-8-hydroxyquinoline complex (AlQ) with two chlorides standing perpendicularly on the graphene sheet, and labeled as the molecular cluster of C38-AlQ. This molecular cluster interacts
65 with one pyrogallol by one hydroxyl group coordinated with aluminum ion, the new molecular cluster labeled as C38-AlQ+py. When the graphene surface was modified by two Aluminum-8-hydroxyquinoline complex (AlQ) with four chlorides by cross-

coordination with each other between aluminum ions and N- or O in the 8-hydroxylquinolines, and labeled as C38-2AlQ. This molecular cluster interacts with one pyrogallol by two neighboring hydroxyl groups coordinated with two aluminum ions, and the formed molecular cluster was labeled as C38-2AlQ+py. All these molecules and molecular clusters were designed by PCMOD software and the structures were further optimized by MOPAC2012 as described about.
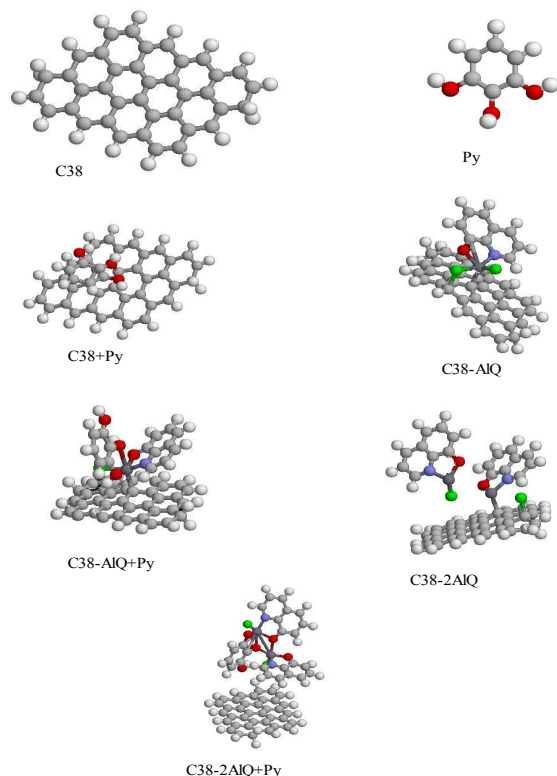

Fig.1 molecule or molecular clusters related to electrochemical catalysis of pyrogallol. C38: graphene with 38 carbon atoms; Py: pyrogallol; C38+Py: graphene of C38 interacted with one pyrogallol; C38-AlQ: graphene of C38 modified with one Al-8-hydroxyquinoline and 2 chlorides; C38-AlQ+Py: graphene of C38 modified with one Al-8-hydroxyquinoline and two chlorides and interacted with one pyrogallol; C38-2AlQ: graphene of C38 modified with 2 of Al-8-hydroxyquinoline and 2 chlorides; C38-2AlQ+Py: graphene of C38 modified with 2 of Al-8-hydroxyquinoline with 2 chlorides and interacted with one pyrogallol.

Quantum chemical computational details

All quantum chemical calculation in this work was performed with semi-empirical quantum chemical methods of MP6 in MOPAC2012 software package[14,15] on personal computer. All molecules and molecular clusters were designed by PCMOD 7.0 and the structures were further optimized with MOPAC2012 software before the calculations in energy and molecular orbital with energy gradient normal drops below 0.01 kCal in heat of formation. The semi-empirical method is not a precise method in quantum chemical calculations as Ab initio, Gauss, but it can give out valuable information about the system in a comparative study with a personal computer in a short time. The heat of formations and frontier orbitals were extracted from the semi-empirical calculations, and used to analyze the stability and the electron transfer properties of each molecular cluster. All the molecules and molecular clusters are calculated in the vacuum condition, and do not considered the influence of solvent on the calculation results, partly due to the calculation complexity and the methyl silicone oil of organic phase mixed with the graphite powder and reduced the influences of polarity of solvents such as water on the molecule and molecular clusters.

Results and discussion

According to thermodynamic principle,[16] the Gibbs free energy change (ΔG_r) of a reaction can be obtained from the enthalpy change (ΔH_r) and entropy change (ΔS_r) of the reaction with heats of formation and entropies of products and reactants included in the reaction calculated with PM6 in thermodynamic model described as the following equation,

$$\Delta G_r = \Delta H_r - T\Delta S_r \tag{1}$$

The enthalpy change and entropy change of the reaction can be calculated with the following formulas,

$$\Delta H_r = \sum_{i=1}^{n} H_{f,i,product} - \sum_{j=1}^{m} H_{f,j,reactant} \tag{2}$$

$$\Delta S_r = \sum_{i=1}^{n} S_{i,product} - \sum_{j=1}^{m} S_{j,reactant} \tag{3}$$

Where n and m are the numbers of products and reactants included in the reaction, respectively. All the thermodynamic data of the related molecules and molecular clusters were listed in **Table 1**. All cluster formation heats show a larger negative values, which imply the formations processes are exothermal, while the entropy changes in the systems are not very larger, so that the reaction free energy would be negative, which indicates that the formation process occurs spontaneously, and the initial states of the systems are very stable with an except of the molecular cluster of C38-2AlQ+Py, which gives a small positive value of 8.6059 kJ/mol.

Table 1 The heat of formation of molecule or molecular cluster.

Molecule or cluster	H_f /kJ.mol^{-1}	S_f /kJ.mol^{-1}	ΔH_r /kJ.mol^{-1}	ΔS_r /kJ.mol^{-1}	ΔG_r /kJ.mol^{-1}
C38	569.09	0.61107			
Py	-421.42	0.36236			
AlQ	759.05	0.69102			
C38-AlQ	54.693	0.83492	-1271.4	-0.21850	-1206.3
C38-2AlQ	-41.689	1.35109	-2041.5	-0.64201	-1850.2
C38+Py	80.078	0.87554	-67.588	-0.09789	-38.417
C38-Alq+Py	-479.12	1.03995	-112.39	-0.40604	8.6059
C38-2AlQ+Py	-702.69	1.15430	-239.58	-0.56047	-72.564

The symbols were as those described in **Fig.1**.

The frontier orbital energy analysis of molecule and molecular clusters

According to quantum chemical theory,[17] each molecule or molecular cluster includes n number of molecular orbitals. Each molecular orbital is linearly combined of m number of valence electron orbitals of the atoms in the molecule or molecular cluster, and described as,

$$\phi_i = \sum_{j=1}^{m} C_{i,j} \varphi_{i,j} \qquad (4)$$

Here Φ_i is the ith molecular orbital, $\varphi_{i,j}$ is atomic valence electron orbital of atoms $c_{i,j}$ is the coefficient of jth atomic orbital in ith molecular orbital and $c_{i,j}^2$ indicates the fractional probability of the jth atomic orbital in the ith molecular orbital, and follows the normalization principle,

$$\sum_{j=1}^{m} c_{i,j}^2 = 1 \qquad (5)$$

The Hamiltonian, $\hat{H}_i$, of the system can be described as,

$$\hat{H}_i = \sum_{j=1}^{m} \hat{h}_j + \sum_{j=1}^{m} V_j \qquad (6)$$

Where $\hat{h}_j$ is the kinetic energy part of the system; V_j is the potential energy part of the system. According to Schődinger equation,

$$\hat{H}_i \phi_i = E_i \phi_i \qquad (7)$$

Where Φ_i is the molecular orbital, E_i is the energy of the molecular orbital.so by performing quantum chemical calculation, we can obtained the energy of system, energy and function of each molecular orbital. According to the Kohn-Sham Theory, the frontier molecular orbital (FMO) composed of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) among the molecular orbitals are very important in description of the chemical reactive tendency of a molecule with approximations, and may be useful for evaluation of electrochemical activity. Some descriptors were theoretical studied and reported such as the frontier orbital gap (ΔE), chemical potential (μ),[18] molecular hardness (η),[19] molecular electron affinity (ω),[20,21] of which the calculated data are not listed in the table 2 and charge exchange (ΔN) from A to B molecules.[22-24] All of these terms can be calculated from the frontier orbital energy of the HOMO (ε_{HOMO}) and LUMO (ε_{LUMO}). All these descriptors are defined as,

$$\Delta E = \varepsilon_{LUMO} - \varepsilon_{HOMO} \qquad (8)$$

$$\eta = \frac{1}{2}\left(\varepsilon_{LUMO} - \varepsilon_{HOMO}\right) \qquad (9)$$

$$\mu = \frac{1}{2}\left(\varepsilon_{LUMO} + \varepsilon_{HOMO}\right) \qquad (10)$$

$$\varpi = \frac{\mu^2}{2\eta} \qquad (11)$$

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A - \eta_B)} \underline{\underline{\text{B:reference point}}} - \frac{\mu_A}{2\eta_A} \qquad (12)$$

Here ΔN was originally describe the electron transfer quantity from molecule A to molecule B, but in our case we describe the electron transfer from molecule A to another electrode or output electric circuit with $\mu_B=0$, $\eta_B=0$, we consider B reference point, and called exchangeable electron. All the molecules and molecular clusters can be calculated by PM6 in MOPAC2012 software, and all the descriptors were calculated and listed in **Table 2**. In order to compare the electron transfer capacity of graphene C38 and modified C38 and other molecular clusters, we used another descriptor ($\Delta\Delta N$), which defined as the difference of the exchangeable electrons between any molecular cluster (ΔN_{MC}) and graphene C38 (ΔN_{C38}), and may be called difference of exchangeable electron as,

$$\Delta\Delta N = \Delta N_{MC} - \Delta N_{C38} \qquad (13)$$

From the table 2 it can be seen that the initial states of the modified CPEs have slightly negative values of exchangeable electrons compared with the C38 graphene, so they are some slightly tendency to accepting electrons from its environment substance.

Table 2.The calculated descriptors of molecule and molecular clusters.

Molecule Or cluster	E_{HOMO}/ eV	E_{LUMO}/ eV	μ/eV	η/eV	ΔN	$\Delta\Delta N$
C38	-7.625	-1.555	4.590	3.037	0.756	0
Py	-8.689	0.099	4.392	4.295	0.511	-0.245
C38-AlQ	-7.511	-1.034	4.273	3.239	0.660	-0.096
C38-2AlQ	-7.289	-1.826	4.558	3.015	0.756	0.000
C38+Py	-7.712	-1.658	4.685	3.027	0.774	0.018
C38-AlQ+Py	-7.386	-1.933	4.660	2.727	0.854	0.098
C38-2AlQ+Py	-7.351	-1.641	4.496	2.855	0.787	0.031
C38+Py$^+$	-10.71	-4.600	7.655	3.055	1.253	0.497
C38-2AlQ+Py$^+$	-10.42	-5.287	7.854	2.567	1.530	0.774
C38+Py^{2+}	-13.097	-6.402	9.746	3.348	1.455	0.699
C38-AlQ+Py^{2+}	-12.184	-6.893	9.539	2.646	1.803	1.047

The terms with"+" indicates the molecular cluster was calculated with one positive charge, the other symbels were as those described in Fig.1.

From the calculation results in the table 2 we can seen that all values from Py to C38-2AlQ+Py are negative or with smaller positive. But after one electron is first drawn out from the system, in the second electron drawn out from the system, the difference of the exchangeable electrons ($\Delta\Delta N$) are became larger positive values of 0.497 for unmodified graphite paste electrode and 0.774 for the modified graphite paste electrode. The value increase as 55.7%. If the calculation results with two positive charges, the exchangeable electrons at the modified CPE is 49.8% increases over the unmodified CPE. This increase value is just accord well the oxidation peak current increase of 53% in the CVs of pyrogallol on modified CPE than that on unmodified CPE in the

previous study.[5] This is an electron- transfer induced oxidation process of pyrogallol on the CPEs. In order to found the reasons of the calculations, we further analyze the components of the frontier orbital of each molecule and molecular cluster.

The frontier orbital component analysis of molecule and molecular clusters

The components of the frontier orbitals of LOMO and HOMO are another main factor to determine the electronic property of the systems, such as electron storage and electron transportation.

In GPE system, all LUMO orbitals of C38 and its modified with or without Py molecular clusters are composed of p_z atomic orbital of carbon atom in C38 graphene, except the C38-2AlQ+Py$^+$ and Py itself, which are composed of s and p orbitals from Alq and Py only. The HOMO orbitals of C38 and modified C38 graphene are composed of p_z atomic orbitals of carbon atom in C38 graphene and nitrogen and oxygen atoms from AlQ as shown in Fig.2. except the Py$^+$ and C38-2AlQ+Py$^+$, they are composed of p or pz orbitals from Py only. In this situation, the electron thransfer from HOMO orbital of Py to the LUMO orbitals of the modified electrode clusters in the electrochemical oxidation process. For the molecular clusters of C38-2AlQ+Py and C38+Py, the HOMO orbitals are composed of pz atomic orbitals from C38 and AlQ. It has nothing to do with Py. For the oxidation of Py, it needs one more electron drwn from the molecular clusters, thi process may be called electron transfer induced electrochemical catalytic oxidation of pyrogallol.
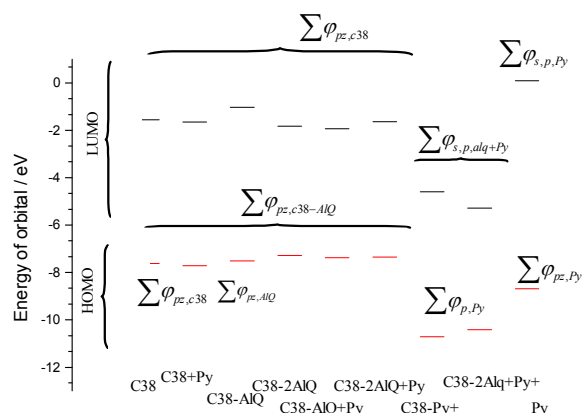

Fig.2 the plot of frontier orbital energy and their components of molecule and molecular cluster. The symbels were as those described in Fig.1.

The relationship between redox potential and energies of frontier orbital

The frontier orbital of HOMO and LUMO are important in chemical reactions, especially in electrochemical reactions of receiving or losing electron from them. So as early as 1949, Maccoll developed a good relation between reduction potential of a conjugated system and the frontier orbital energy.[25] The oxidation potential, E_{OX}, is proportional to the energy of HOMO, E_{HOMO}, and the reduction potential E_{RED} is proportional to the energy of LUMO, ε_{LUMO}, and all together the expression can be written as,[26]

$$E_{OX/RED} = a + b\varepsilon_{HOMO/LUMO} \qquad (14)$$

Where $E_{OX/RED}$ is the experimental potentials of oxidation and reductions, and a, and b are constants. According to this theory, the two molecular clusters C38+Py and C38-2AlQ+Py were chosen for the electrochemical redox reactions at unmodified CPE and modified CPE. The first oxidation peak potential of modified CPE of 0.448 V is related to the energy of HOMO of C38-2AlQ+Py molecular cluster, the second oxidation peak is not obvious, and the third oxidation peak of 0.883 V is related to the HOMO of molecular cluster of C38-2AlQ+Py+. In unmodified CPE, the first oxidation peak potential of 0.507 V related to the energy of HOMO of C38+Py molecular cluster, and the second oxidation peak potential of 0.886 V related to energy of HOMO of C38+Py+ molecular cluster. The reduction peak potential of 0.162 V is related to the energy of LUMO of molecular cluster C38+Py for unmodified CPE, and reduction peak potential of 0.146 V is related to the energy of LUMO of molecular cluster of C38-2AlQ+Py for the modified CPE, respectively. The plot of redox peak potentials against the energies of frontier orbital is a good linear equation was obtained as shown in **Fig.3** with the regression equation of ,

$$E_{p,redox}/V = 0.0156(\pm 0.034) + 0.0669(\pm 0.004) E_{H/L}/eV$$
$$R^2 = 0.986, SD = 0.044$$

$$(15)$$

This linear relationship of experimental peak potential and calculated frontier orbital energies further indicates that the quantum chemical calculations are accord well with the experimental results, and it offers a theoretical evidence for the electro-catalytic behavior of pyrogallol at the 8-hydroxylquinoline-alminium complex modified CPE.
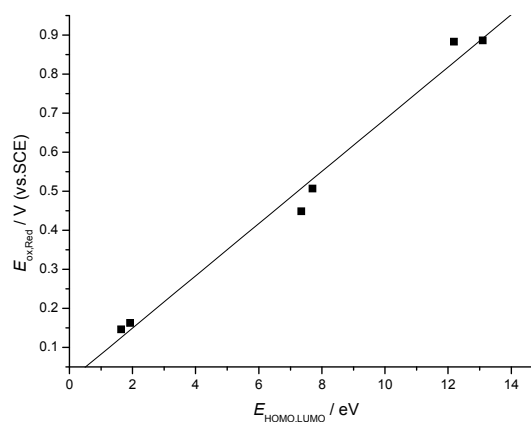

Fig.3 The relationship between redox potential and energy of frontier orbital

The qualitative explanation of the catalysis mechanism

The Alq modifier is responsible for the solid phase micro extraction and electron transfer in catalytic oxidation of pyrogallol molecule, which not only stabilizes the pyrogallol, but

also the intermediates of the oxidation processes.

The adsorption process of pyrogallol on the 8-hydroxyquinoline-aluminum modified carbon electrode [5] may be described as the scheme 1. One pyrogallol molecule adsorbed on the modified CPE interacts with modifier by two near-by phenol groups with two aluminium ions, and leaves one phenol for the first electrochemical oxidization.This result is accord well with thermodynamic calculation results with -72.564 kJ/mol of the changes of Gibbs free energy for the reaction. This interaction results in the second and third oxidation peak potentials shift to positive direction in the CVs.
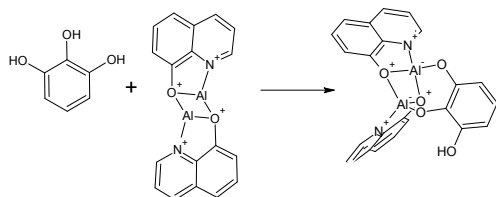
Scheme 1   The adsorption pyrogallol at the modified carbon paste electrode

Conclusions

In the present paper, semiempirical quantum chemical method of PM6 in MOPAC2012 software was used in quantum chemical calculations based on the molecular cluster models including graphene with 38 carbon atoms, aluminum-8-hydroxylquinoline complexes and pyrogallol for electrochemical catalytic oxidation of pyrogallol at aluminium-8-hydroxylquinoline complexes modified carbon paste electrode. The results indicated that the designed molecular cluster models are stable from the thermodynamic view. The catalytic behavior comes from electron transfer induced catalytic electrochemical oxidation by analysis of frontier orbital energy and composited components. The difference of exchangeable electron of pyrogallol at modified carbon paste electrode is about 55.7% larger than that at unmodified carbon paste electrode, which is accord well with the increase of oxidation peak current at corresponding electrodes about 53%. The quantum chemical calculation will help us to well understand the electrochemical catalytic behavior of the systems as well as the adsorption mechanism.

Acknowledgements

Notes and references

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