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# TUNING THE CATALYTIC PROPERTY OF Pt/GRAPHENE USING SMALL ORGANIC MOLECULE

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***Abstract-*** ***We attempt to detect the possibility to modify the catalytic property of Pt/graphene using small organic molecule. Results of density functional theory calculations show that ssDNA segment and L-leucine modify the electron transfer at the interface, changing the electronic property and redox property of Pt/graphene catalyst system. L-leucine promotes electron transfer from Pt and increases the HOMO and LUMO of L-Pt/G system, while ssDNA segment lessens electron transfer from Pt and increases the HOMO and LUMO. With such electronic properties, L-leucine is beneficial to enhance the*** activity ***of Pt/graphene for catalytic α-dehydrogenation of ethanol while ssDNA fragment has adverse effects on the catalyzed α-dehydrogenation of ethanol. Reults will favour the design of active next-generation catalyst based on metal/graphene composite for novel applications.***

***Keywords -*** Graphene; ethanol decomposition; Pt; DFT

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## I. INTRODUCTION

Graphene, due to its extraordinary properties [1], has inspired a flurry of interests for both fundamental science and applied research. Graphene-based nanoparticle catalyst exhibits superior property in catalysis fields. However, the π - π interaction between aromatic rings of the graphene is inclined to make graphene-based catalyst agglomerating in solution. Further functionalization and dispersion of graphene-based catalyst are of crucial importance for their end applications. Covalent and noncovalent modification can prevent the agglomeration of graphene-based catalyst [2-15]. Introducing specific functional groups with the help of covalent chemical modification contributes to the stable dispersion of graphene-based catalyst, which leaves permanently destroy to the graphene. However, non-covalent chemical modification can avoid permanently destroy to the stable structure of graphene, which can be reduced at the same time [12-15].

Recently, further non-covalent functionalized graphene-base catalyst is getting increasing attention. Non-covalent functionalization can modify the graphene-based catalyst. For instance, nitrobenzene can modify electron transfer between graphene and the supported nano-particle [16,17]. 3,4,9,10-perylene dianhydride self-assemble on graphene, forming ordered molecular structure and guiding the deposition of metal (metal oxide) nanoparticles at special sites [18,19]. DNA non-covalent modified graphene-based Au nanoparticle can realize the even dispersion of Au on two dimensional composite material due to the interaction between the sulfhydryl on DNA strand and Au nanoparticle, which enhances the dispersion of graphene-based catalyst in solution and avoiding the permanent structure destruction of grapheme [20-26,]. Amino acids also have been introduced to modify graphene for advanced applicaations [27-31]. Bovine serum albumin (BSA) modified graphene can act as ideal carrier, on which heterogeneous metal nanoparticles can efficiently self-assemble at its specific sites forming various composite material respect to structure, size and shape [32]. However, structure transformation and new interface introduction can usually turn the properties of the graphene-based multi-phase catalyst system has not been studied systematically, hence the specific purpose-guided modification is also poorly understood.

In this work, two kinds of small organic molecules related to two representative types of organic species in research DNA and protein were selected to non-covalent modified graphene-base Pt nanocatalyst, with the view of electron donor and acceptor, one is L-leucine (branched-chain amino acids and one of the 20 common amino acids with two unsymmetrical carbon atoms and soluble to water), the other is ssDNA fragment with two bases (G and C). Density functional theory calculations and molecular dynamic simulations were performed to discuss the electronic properties of Pt/graphene system, Pt-leucine/graphene system, and Pt-ssDNA/graphene system, and the interface effect on the electronic properties, ethanol adsorption, and catalyzed α-dehydrogenation of ethanol, getting deeper insight into the synergetic catalytic property of organic molecule modified graphene based metal nanoparticles.

## II. CALCULATION METHOD

All calculations were performed using the spin-unrestricted density functional theory (DFT) as implemented in the DMol3 code [33,34]. The exchange-correlation functions were computed within a uniform generalized gradient approximation (GGA) with the revised Perdew−Burke−Ernzerhof (RPBE) [35]. The all electron relativistic (AER) procedure [36], which includes all core electrons explicitly and introduces some relativistic effects into the core, was used for the core treatments. In addition, double numerical plus polarization (DNP) was chosen as the basis set with an orbital cutoff of 5 Å. A combination of linear synchronous transit (LST) and quadratic synchronous transit (QST) method was used to search the transition states of reactions [37].

A platinum cluster with 4 Pt atoms was supported on a hexagonal graphene containing 204 C atoms, which was denoted as Pt/G. After optimization of Pt/G, a ssDNA segment with two base (G and C) and L-leucine were introduced to combine with Pt/G to obtain DNA-Pt/G system and L-Pt/G system. Then geometric optimizations for DNA-Pt/G and L-Pt/G were performed to reach theirs stable configuration. To investigate the synergetic effect of ssDNA and L-leucine on the catalytic properties of Pt/G, the adsorption modes of ethanol and several of its dehydrogenation products on Pt/G, DNA-Pt/G and L-Pt/G were calculated, and the reaction energies as well as activation barriers of $\alpha$-dehydrogenation.

The combination energy $E_{\mathrm{bind}}$ between the Pt cluster and G [ssDNA/G and L/G] was defined as

$$E_{\mathrm{bind}}=\mathrm{E}_{\mathrm{cat.}}-(E_{\mathrm{Pt.}}+E_{\mathrm{G\text{-}based}}) \qquad (1)$$

where the subscripts $E_{\mathrm{cat.}}$, $E_{\mathrm{Pt}}$, and $E_{\mathrm{G\text{-}based}}$ denoted the total energy of the catalyst system (Pt/G, L-Pt/G, and DNA-Pt/G), the energy of the Pt cluster, and the energy of L-Pt/G [DNA-Pt/G], respectively.

The adsorption energy Ead between the ethanol and Pt/G [DNA-Pt/G and L-Pt/G] was defined as

$$E_{\mathrm{ad}}=E_{\mathrm{tol.}}-(E_{\mathrm{cat.}}+E_{\mathrm{ethanol}}) \qquad (2)$$

where the subscripts $E_{\mathrm{tol.}}$, $E_{\mathrm{cat.}}$, and $E_{\mathrm{ethanol}}$ denoted the total energy of adsorption system, and the energies of the corresponding substances.

## III.RESULTS AND DISCUSSION

### Structure and electronic property of catalysts

Fig. 1 illustrates the stable configurations of Pt/G, L-Pt/G, and DNA-Pt/G. The related combination energy $E_{\mathrm{bind}}$/per Pt atom for Pt/G, L-Pt/G, and DNA-Pt/G, the minimum distance ($L_{\mathrm{D}}$) between Pt and catalyst surface, and the electron charge transfer ($Q_{\mathrm{t}}$) from Pt cluster to catalyst, are listed in Table 1. The $E_{\mathrm{bind}}$/per Pt atom for Pt/G, L-Pt/G, and DNA-Pt/G are -2.254 eV, -3.361 eV, and -1.046 eV. According to $E_{\mathrm{bind}}$, L-leucine increases the stability of Pt cluster supported on graphene, while DNA segment decreases the stability of Pt cluster on graphene. $L_{\mathrm{D}}$ for Pt/G, L-Pt/G, and DNA-Pt/G are 2.316 Å, 2.274 Å, and 2.274 Å, respectively. Through L-leucine and DNA segment shorten the distance between Pt cluster and graphene surface, only L-leucine enhances electron transfer from Pt cluster while DNA segment lessen the electron transfer, which shows the $Q_{\mathrm{t}}$ of 0.228, 0.457, and 0.201, for Pt/G, L-Pt/G, and DNA-Pt/G, respectively. $E_{\mathrm{bind}}$ is in proportion to $Q_{\mathrm{t}}$, which implies that host-gust electronic interaction is the determinant to the stability of such composites.

More positive charge population on Pt cluster in L-Pt/G system should be related to the electron accepting ability of L-leucine, as shown in Fig. 1, where L-leucine accepts 3.221 *e*. However, though ssDNA segment acts as electron acceptor with minor negative charge population, ssDNA segment can inhibit electron transfer between Pt and graphene. In addition, both L-leucine and ssDNA segment are physisorbed on graphene, corresponding to the results of our previous works [38].

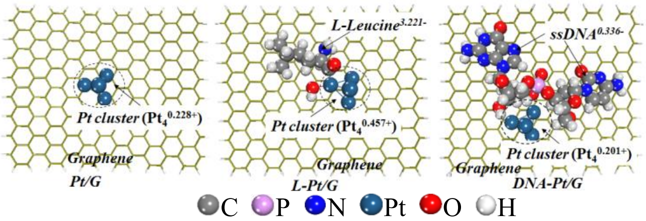

Fig. 1 Stable configurations of Pt/G, L-Pt/G, and DNA-Pt/G

TABLE 1 Combination energy $E_{\mathrm{bind}}$/per Pt atom for Pt/G, L-Pt/G, and DNA-Pt/G, the minimum distance ($L_{\mathrm{D}}$) between Pt and catalyst surface, and the electron charge transfer ($Q_{\mathrm{t}}$) from Pt cluster to catalyst.

| | $E_{\mathrm{bind}}$/per Pt atom (eV) | $L_{\mathrm{D}}$ (Å) | $Q_{\mathrm{t}}$ (*e*) |
|---|---|---|---|
| Pt/G | -2.254 | 2.316 | 0.228 |
| L-Pt/G | -3.361 | 2.274 | 0.457 |
| DNA-Pt/G | -1.046 | 2.274 | 0.201 |

Fig. 3 illustrates the LUMO and HOMO graphs of Pt/G, L-Pt/G, and DNA-Pt/G. As can be seen from Fiure 3, the HOMO and LUMO of Pt/G are -3.771 eV and -3.681 eV; the HOMO and LUMO of L-Pt/G are the highest as -3.501eV and -3.681eV; the HOMO and LUMO of DNA-Pt/G are the lowest as -4.013eV and -4.003eV. The chemical activity of L-Pt/G will be higher than that of Pt-graphene while the chemical activity of DNA-Pt/G will be lower than that of Pt-graphene.

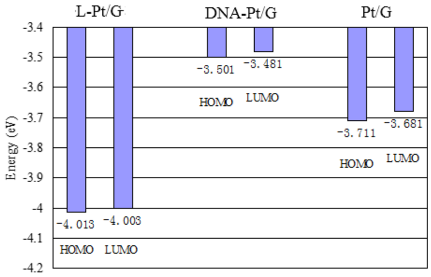

Fig. 2 HOMO and LUMO energies for Pt/G, L-Pt/G, and DNA-Pt/G.

### Adsorption of ethanol on catalysts

Given the fact that DNA-graphene and protein-graphene composite are of excellent electrochemical sensing propertie [20-32], catalytic ethanol decomposition is selected to study the catalytic property of such graphene based Pt nanoparticles catalyst modified by small organic molecule.

As the first step of the heterogeneous catalytic reactions, the adsorption of ethanol on Pt/G, L-Pt/G, and DNA-Pt/G is discussed. Fig. 3 presents the stable adsorption configuration of the adsorption systems. The surface adsorption energy of ethanol on Pt/G, L-Pt/G, and DNA-Pt/G is -0.382 eV, -0.386 eV and -0.450 eV. The interaction between ethanol and DNA-Pt/G is the strongest, and the interaction between ethanol and Pt/G is the weakest. In this way, the catalytic property of Pt-graphene can be regulated by different organic molecule.

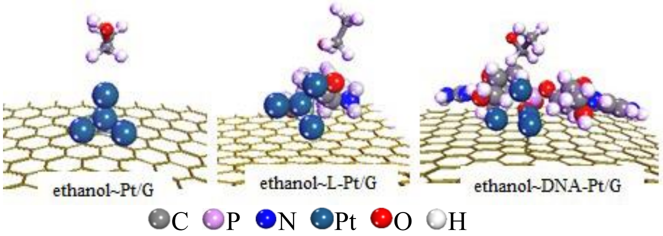

Fig. 3 Stable configurations for ethanol adsorption on Pt/G, L-Pt/G, and DNA-Pt/G

TABLE 2 $E_{ad}$ for ethanol~Pt/G, ethanol~L-Pt/G, and ethanol~DNA-Pt/G, the minimum distance ($L_D$) between ethanol and Pt, and the electron charge transfer ($Q_t$) from ethanol to catalyst.

| | $E_{ad}$ (eV) | $L_D$ (Å) | $Q_t$ ($e$) |
|---|---|---|---|
| ethanol~Pt/G | -0.382 | 2.316 | 0.228 |
| ethanol~L-Pt/G | -0.586 | 2.274 | 0.457 |
| ethanol~DNA-Pt/G | -0.350 | 2.274 | 0.201 |

### Catalytic reaction for $\alpha$-dehydrogenation of ethanol

During Pt-catalyzed decomposition of ethanol, the decomposition of $\alpha$-H of ethanol is energetically accessible. Hence, the adsorption and decomposition of $\alpha$-H of ethanol is selected as the probe reaction to compare the catalytic activity of Pt/G, L-Pt/G, and DNA-Pt/G. Fig. 4 illustrates the energy profile of $\alpha$-dehydrogenation of ethanol catalyzed by Pt/G, L-Pt/G, and DNA-Pt/G. As can be seen from Fig. 4, the $\alpha$-H decompositions of ethanol on Pt/G, L-Pt/G, and DNA-Pt/G are exothermic process. The activation energy ($E_a$) for Pt/G catalyzed $\alpha$-dehydrogenation of ethanol, L-Pt/G catalyzed $\alpha$-dehydrogenation of ethanol, and DNA-Pt/G catalyzed $\alpha$-dehydrogenation of ethanol, are 0.518eV, 0.433eV, and 0.853eV, respectively. L-Pt/G catalyzed $\alpha$-dehydrogenation of ethanol is easier than both Pt/G catalyzed $\alpha$-dehydrogenation of ethanol and DNA-Pt/G catalyzed $\alpha$-dehydrogenation of ethanol.

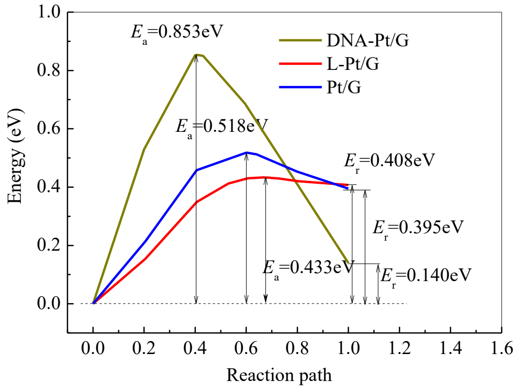

**Fig. 4** Energy profiles for the $\alpha$-dehydrogenation reactions catalyzed by Pt/G, L-Pt/G, and DNA-Pt/G

Results of the reaction kinetics, adsorption energy calculation and electronic property analysis are in good accordance. L-leucine increases the energy of HOMO and LUMO of the catalyst system, while ssDNA decreases the energy of HOMO and LUMO of the catalyst system. ssDNA fragment has adverse effects on the catalyzed $\alpha$-dehydrogenation of ethanol, L-leucine is beneficial to enhance the performance of Pt/graphene. Organic molecule can tuning the electronic property of such host-guest catalyst composite hence regulating the catalytic reaction activity and selectivity. Macromolecule tuning graphene-base catalyst will be discussed in our future works.

## CONCLUSIONS

In this paper, we have reported a theoretic study on tuning the catalytic property of Pt/graphene using ssDNA segment and L-leucine. The electronic properties of Pt/G, L-Pt/G, and DNA-Pt/G were discussed firstly, which shows that host-gust electronic interaction is the determinant to the stability and chemical activity of such composites. L-leucine enhances electron transfer from Pt cluster while DNA segment lessen the electron transfer. The Stronger electronic interaction happening in the L-Pt/G system increases the HOMO and LUMO of L-Pt/G, while compared to the cases for Pt/G system and DNA-Pt/G system. ssDNA segment and L-leucine modified the electronic properties of Pt/G and hance tuning the catalytic activity of Pt/G for $\alpha$-dehydrogenation of ethanol, which will hence affect the catalytic selectivity of Pt/G. Our work will favour the design of active next-generation catalyst based on metal/graphene composite for novel applications.

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