Research Article

Interactions between the Aryldiazonium Cations and Graphene Oxide: A DFT Study

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Understanding the grafting behavior of the aryldiazonium cations is of fundamental and also of practical importance for the vast number of applications that involve the use of modified graphene oxide (from simple adsorption process to electronic and photovoltaic applications). In this work, the mechanism of the adsorption and grafting of diazonium cations on the graphene oxide surface was investigated by the use of density functional theory. Two types of aryldiazonium cations, one bearing only phenyl ring and the other nitrophenyl, were selected as adsorbates/granted moiety. By evaluating the adsorption energies at 7 different positions onto the graphene oxide both in the gaseous and solvent phase (using COSMO approach), the most probable adsorption sites were found. Moreover, the most stable adsorption sites were used to calculate and plot NCI (noncovalent interactions). The obtained results are important as they not only give molecular insights regarding the nature of the interaction and its dependence on the adsorption site of the graphene oxide surface but also on the activation energy for such a grafting reaction to take place, providing a mechanistic aspect to understand these grafting reactions.

1. Introduction

Aryldiazonium cations have been widely applied in the surface modification reaction since the first pioneering work of Prof. Pinson in the 90s [1]. The use of aryldiazonium cations in contrast to other molecules used generally for modification reactions (thiols, silanes, phosphonic acids, etc.) [2] represents the most straight forward strategy to achieve surface modification of materials regardless of their chemical composition nor their conductivity, a feature that is lacking in the case of other molecules (i.e., although thiols offer an elegant way to achieve modification of noble metals, they are not applicable for surface modification of polymers (similar case stand for phosphonic or silanes which are applicable only in the case for surfaces that contain oxyhydroxy groups)) [3]. To date, the grafted layers derived through electrochemical [1, 3–6], sonochemical [7], or thermal dediazonation reactions have been characterized by a vast number of analytical methods (RBS, Tof-SIMS, XPS, IRRAS, AFM, TGA, etc.) [3]. The practical reasons why the modification of the graphene oxide surface through the use of aryldiazonium cations was performed were to give the

material nanocarrier ability for the delivery of anticancer drugs [8], to improve its nonlinear optical performance [9], to influence the structure/property relationship in its nanocomposites with iron oxide nanoparticles [10], etc. In comparison with experimental methods, there is a lack of theoretical studies applied to understand the grafting/adsorption of the aryldiazonium cations onto the graphene oxide. In the current study, we address the adsorption of the aryldiazonium cations, their binding energy, and the activation energy related with their grafting onto the graphene oxide by using DFT calculations.

2. Computational Details

The adsorption properties of aryldiazonium cations on graphene surfaces are investigated by the DFT method using the generalized gradient approximation (GGA) [11] or PBE [12–15]. The graphene oxide (GOx) model is approximated by using a 5×5 graphene model that contains epoxy, hydroxyl, and carboxy groups on its surface (Figure 1(a)).

While the model takes into account the influence of the different functional groups of the GOx surface onto the

FIGURE 1: (a) Adsorption site positions for diazonium structures (P1–P5: flat lying onto the GOx surface; P6 and P7: perpendicular to the diazonium group oriented towards the GOx surface) and (b) the computed adsorption energies (in vacuum and water) of aryldiazonium cations onto the different GOx adsorption sites.

adsorption and the grafting of the aryldiazonium cations, the effect of the concentration of such surface groups is not considered in this work. This can also have an influence on the adsorption properties of the studied molecules [16, 17] but probably not an extensive impact during the grafting reaction of such moieties onto the GOx surface [3]. As already observed by the De Feyter group [18], the grafting of the aryl radical proceeds in mushroom-type (one root, many branches and leaves) of film formation, meaning that the whole surface is not completely covered with the aryl groups and that the radicals (responsible for the initial grafting) prefer to react with the first grafted group rather than with the surface; that is, the reaction is no more a surface reaction.

The calculations were based on the double-numeric quality with polarization functions (DNP) basis set [19, 20]. The calculations in water were performed using Conductor-like Screening Model (COSMO) [21].

The adsorption energy, both in vacuum and water models, is evaluated as follows [6, 13, 20]:

$$E_{\text{interaction}} = E_{\text{GOx-diazonium}} - (E_{\text{GOx}} + E_{\text{diazonium}}), \quad (1)$$

where $E_{\text{GOx-diazonium}}$ is the total energy of the adsorption system. E_{GOx} and $E_{\text{diazonium}}$ are the energies of the isolated graphene oxide and aryldiazonium cations, respectively. The transition state (in water) is computed using the combination of linear synchronous transit (LST) and quadratic synchronous transit (QST) [22].

3. Results and Discussion

Although the adsorption of the diazonium salts onto the metal surface is evidenced experimentally from corrosion measurements in the case of iron [3], the interaction

energies, adsorption geometry, and the interaction type between the GOx surface and the aryldiazonium cations remain up to now unknown for the GOx surface. For the gold surface, the calculated bond dissociation energy (BDE) of the grafted aryl or alkyl moiety is ≈ 40 kcal/mol [6, 12]. The adsorption of the diazonium cation is the first step for the grafting reaction. In order to evaluate and understand the adsorption of the diazonium cations (and the substituent effect) onto the GOx surface, different adsorption sites were explored (Figure 1(a)). The calculated adsorption energies (Figure 1(b)) are in the range of -40 up to -60 kcal/mol in the case of vacuum and -22 up to -45 kcal/mol when the effect of the solvent is accounted. In all cases, the highest adsorption energies were obtained for the P5 adsorption position—when the aryldiazonium cations are adsorbed planary onto the phenyl rings of the GOx surface. The adsorption energy for the phenyldiazonium cation is -45 kcal/mol, a value that is slightly higher (nearly -5 kcal/mol) than the adsorption energy of nitrophenyldiazonium cation. This suggests that the interaction mode is mainly a π - π stacking one [23], so probably, the reason of the slightly lower adsorption energy for the nitrophenyl cation is the distortion of its planarity, decreasing its π stacking ability with the GOx surface.

To assess correctly the interaction type [24], the NCI (noncovalent interaction) plot and the reduced density gradient (RDG) vs. $\text{sign}(\lambda)\rho$ were computed [25] for the highest adsorption site. The visualization of the NCI surface (Figure 2(a)) and the RDG vs. $\text{sign}(\lambda)\rho$ supports that the adsorption interaction is a van der Waals one. The decreased adsorption energy for the nitrophenyl cation in comparison to the phenyl one is due to the repulsion interaction (this is evident in Figure 2, the plot part at the region of the 0.02 $\text{sign}(\lambda)\rho$ value).

FIGURE 2: Noncovalent interaction surfaces (a) ((A) phenyldiazonium cation; (B) nitrophenyldiazonium cation) and (b) the plot of reduced density gradient (RDG) vs. $\text{sign}(\lambda)\rho$ for the interaction of $\text{GOx/N}_2^+\text{-Ph}$ (red) and $\text{GOx/N}_2^+\text{-Ph-NO}_2$ (black).

FIGURE 3: (a) Grafting positions (G1–G3) and (b) computed BDEs in vacuum and water (COSMO) for the bonding of phenyl radicals and nitrophenyl radicals at 3 distinctive grafting positions onto the GOx surface.

The dissociation energy for the grafted aryl groups is calculated for three different possible grafting positions (Figure 3, G1 to G3). The computed BDE values indicate that the most probable grafting position is at G3, which correlates well with the adsorption energy results as this is also the preferred adsorption site. The BDE in the case of solvent is ≈ 66 kcal/mol (Figure 3(b)).

The homolytic bond scission energy for the aryldiazonium cations (at 0 K) ($\text{ArN}_2^+ \rightarrow \text{Ar}^* + \text{N}_2$) for the studied molecules, together with their corresponding transition states in the grafting reactions on the graphene oxide surface, is presented in Figure 4. The BDE for the phenyldiazonium cation is 32.4 kcal/mol and for the nitrophenyldiazonium cation is 36.1 kcal/mol. Spontaneous grafting of the

FIGURE 4: Graph of homolytic BDE of (a) phenyldiazonium and (b) nitrophenyldiazonium cations together with the corresponding TS search energy trajectories for the grafting reaction of (c) phenyl radicals and (d) nitrophenyl radicals onto the graphene oxide surface.

aryldiazonium salts on different bulk or nanoscopic carbons is well known [3]. Thus, in order for the grafting reactions to take place spontaneously, a plausible route will be initiated through the instability of aryldiazonium cations. The grafting reactions after their initiations are sustained by the energy gain from the difference between the reaction energy (-37.86 kcal/mol phenyl radical, -39.76 nitrophenyl radical) and the energy barrier for the grafting reaction (35.28 kcal/mol for phenyldiazonium and 38.41 kcal/mol nitrophenyldiazonium) to take place.

4. Conclusion

In this work, the adsorption, grafting, and activation energy of aryldiazonium cations onto the graphene oxide surface

were studied. The adsorption energy results showed that the interaction strength is up to -45 kcal/mol, pointing out to chemisorption. The adsorption of these cations onto the graphene oxide is through the van der Waals interactions. The bond dissociation energy for the grafted layer is high (≈ 66 kcal/mol), showing that the formed interface is quite stable. Comparing the BDE value for the scission of diazonium cation to its radical, with the values of the energy barrier and the reaction energy, it supports that the grafting reaction for this substrate is barrierless, meaning that the grafting reaction will proceed with the adsorption of the diazonium cation, nitrogen bond section, and the grafting of the formed aryl radical. This work will contribute to the detailed molecular understanding of the adsorption/grafting chemistry of the aryldiazonium cations, respectively, and

aryl radicals onto graphene oxide and other graphene-like materials.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

Part of the results was presented at the 25th Congress of SCTM.

Conflicts of Interest

The author declares that there are no conflicts of interest.

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