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REVIEW ARTICLE

Computational Exploration of Functional Nanoscale Carbonaceous Materials

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Abstract: ***Background***: The unique ability of carbon to form a wide variety of allotropic modifications has ushered in a new era in material science. Tuning the properties of these materials by functionalization is a must-have tool for their design customized for a specific practical use. The exponentially growing computational power available to researchers allows for the prediction and thorough understanding of the underlying physicochemical processes responsible for the practical properties of pristine and modified carbons using the methods of quantum chemistry.

Methods: This review focuses on the computational assessment of the influence of functionalization on the properties of carbons and enabling desired practical properties of the new materials. The first section of each part of this review focuses on graphene with nearly planar units built from sp^2-carbons. The second section discusses patterns of sp^2-carbons rolled up into curved 3D structures in a variety of ways (fullerenes). The overview of other types of carbonaceous materials, including those with a high abundance of sp^3-carbons, including nanodiamonds, can be found in the third section of each manuscript's part.

Conclusion: The computational methods are especially critical for predicting electronic properties of materials such as the bandgap, conductivity, optical and photoelectronic properties, solubility, adsorptivity, the potential for catalysis, sensing, imaging, and biomedical applications. We expect that introduction of defects to carbonaceous materials as a type of their functionalization will be a point of growth in this area of computational research.

Keywords: Computation, functionalization, carbonaceous materials, graphene, nanomaterial, allotropic modifications.

1. INTRODUCTION

The unique ability of carbon to form a wide variety of allotropic modifications has ushered in a new era in material science, which resulted in the Nobel Prizes for the discovery of fullerenes [1] and graphene [2]. The carbonaceous components are common building blocks of novel materials with applications ranging from catalysis to drug delivery. Graphene-based electrodes brought tremendous improvement in energy storage devices, replacing traditional heavyweight, costly and transient cycle life electrodes with flexible, high performance, cost-effective, and long-lasting cycle life ones [3-5]. Tuning the properties of these materials by functionalization is a must-have tool for their design customized for a specific practical use. On the other end, the exponentially growing computational power available to researchers allows for the prediction and thorough understanding of the underlying physicochemical processes responsible for the practical properties of pristine and modified carbons using the methods of quantum chemistry. The purpose of this review is to explore the recent advances in the computational chemistry of carbonaceous materials as a toolbox for further design of the experimental methods of their functionalization, characterization, and customization for the wide range of practical applications in modern technology.

The first part of this review focuses on the computational assessment of the influence of functionalization on the properties of carbons, which is a starting point for the design of new materials. Therefore, we look at the modifications that enable certain practical material properties and refer to such modifications as "functionalizations". Once we know what type of functionalization would bring about the desired properties, we need to experimentally perform the functionalization and lay the ground for this by computational modeling of its process, which is discussed in the second part of the manuscript. The third part deals with further functionalization of already functionalized carbons and takes advantage of the potential ability of a functional group to facilitate the introduction of other groups of interest.

The first two parts of the manuscript are divided into three sections, each devoted to a specific type of carbon atom in the material and its way of making up a 3D structure. The first section focuses on graphene, which has nearly planar

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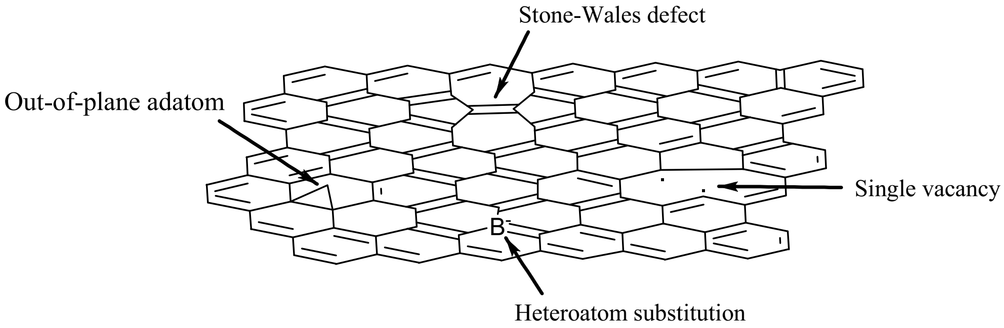

Fig. (1). Structure and examples of defects of a 2D-graphene sheet. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

units built from sp^2-carbons. The **second section** discusses patterns of sp^2-carbons rolled up into curved 3D structures in a variety of ways (fullerenes). The overview of other types of carbonaceous materials, including those with a high abundance of sp^3-carbons, including nanodiamonds, can be found in the **third section** of each manuscript's part.

2. FUNCTIONALIZED CARBONS

2.1. Functionalized Graphene

Graphene is a material made of a single or several 2D sheets of sp^2 carbons usually accompanied by various types of defects (Fig. **1**) [6]. Both the type and distribution of defects as well as the interaction between 2D sheets profoundly affect the physicochemical properties of graphene.

The natural ability of the extended conjugated network of sp^2 carbons in a graphene sheet prompted a computational study that will help develop better insulating materials for high voltage electric cables [7]. The team explored how doping of single vacancy graphene with B, N, and Si and epoxidation of graphene influences its ability to intercept electrical charges and prevent electrical treeing in cross-linked polyethylene insulators. The electronic structures of pristine and modified graphenes were calculated using the spin-polarized density functional theory (DFT) calculations with the Perdew–Burke–Ernzerhof (PBE) functional [8] with Vienna Ab initio Simulation Package (VASP) by the projected–augmented wave (PAW) method [9, 10]. It is found that doped graphene oxides have strong adhesion to the polymer matrix and relatively low chemical activity, which are preferred qualities for suppression of electrical treeing and degradation of the polymer matrix. The Nobel Prize-winning DFT theory became a gold standard for quantum chemistry computational studies of extended structures like graphene. In this review, utilization of the DFT theory will be implied unless specified otherwise.

Interestingly, doping of $-OH$ or $-NH_2$ - functionalized graphene with B and N substantially affects its interaction with four amino acids [11]. However, this effect is much less pronounced for $-COOH$ - functionalized graphene. This difference is attributed to H-bonding that can be tuned by the solvent, providing an opportunity for the design of selective protein sensors. This computation was performed on the GAUSSIAN09 platform [12], using the PCM model to account for the solvent effect.

Calculations performed by the SIESTA code [13] have shown that partial hydrogenation of graphene allows to systematically change its bandgap, providing another tool to design semiconductors for optoelectronic devices [14]. The bandgap of graphene can also be energetically tuned by cycloaddition of various quantities of carbenes [15]. Adsorption of methane and carbon dioxide on edge-functionalized graphene was examined using the Quantum-ESPRESSO program [16]. It was shown that the presence of the $-NH_2$, NO_2, $-COOH$, and $-H_2PO_3$ groups increased adsorption of both methane and carbon dioxide while highly selective effective adsorption of these gases remains a challenge [17]. According to GAUSSIAN09-based computations, functionalization of the edge "dangling" bonds with alkyl, alkenyl, and alkynyl groups affects the bandgap and electron delocalization in the graphene benzene rings [18]. Another SIESTA [13] computation examined the role of vacancy defects as well as B, N, P, and S dopants on the interaction of graphene with the atoms of Na [19]. It was found that the vacancy and dopant defects attract hydroxy-groups; therefore, the control of oxidation plays a critical role in the performance of graphene-sodium batteries [19].

Doping of graphene with Al substantially increases its interaction with a series of halomethanes, moving its energy from the physisorption to the chemisorption region [20]. The presence of a vacancy defect in graphene substantially increases its ability to adsorb Hg, keeping the energy of adsorption in the area of physisorption [21]. Doping the vacancy with Al further improves adsorption of Hg, pushing it to the area of chemisorption [21]. The Pd atoms in Pd-doped graphene retain their ability to adsorb H_2, activating the molecule for several reactions [22]. Therefore, doping of graphene opens the door for the design of graphene-based sensors and catalysts. For example, graphenes doped by Fe or Pt by adsorption are able to effectively adsorb H_2S and catalyze its dissociation to S and H_2 [23] according to the DMol [24] calculations. A group from Argentina reports that defective graphene catalyzed the decomposition of H_2O_2 much more efficiently than pristine graphene because the defective sites better accept the OH-groups without the need of rearranging the carbonaceous surface. Functionalization of the defective sites by carboxy groups further improves the catalytic activity [25]. Embedding atoms of Ge or Ga into the vacancy defects of graphenes is likely to enable the material to catalyze the reduction of N_2O by CO, with Ge being more promising [26].

Due to the higher reactivity of the defective sites, the introduction of defects to graphene can be considered as another method of its functionalization. A variety of DFT-based methods led to the consistent result that the formation of addition or vacancy defects requires a high energy barrier. In the case of multilayered graphite, the vacancy defects tend to interact with interstitial defect atoms forming a perfect graphene domain [27]. The core binding energies consistent with the XPS experiments have been calculated for pristine and defective graphene functionalized with hydrogen- and oxygen-based sorbates [28], using the GPAW simulation package [29].

An efficient application of defected graphene was explored by Huang *et al.* [30], where they investigated a facile mechanism of converting N_2 to NH_3. They predicted that the magnetic moment of a single Fe atom placed on a single vacancy defect of graphene could tune the catalytic conversion of N_2 to NH_3, pointing at a possible alternative to the traditional Haber-Bosch process. Yang *et al.* have predicted that intercalation of Na in the bilayer graphene with vacancy and Stone-Wales defects is more favorable than simple adsorption of Na, which could improve tuning formation energies, electronic and magnetic properties as well as migration energy barriers in the new materials for energy storage and nanomagnetic devices [31].

2.2. Functionalized Fullerenes

The simplest types of fullerenes are cage-like structures of nearly spherical shape (buckyballs), of which C_{60} is among the most common examples. Elongation of a buckyball in one direction brings us to single-wall carbon nanotubes (SWCNT) with closed ends, which can be either metallic or semiconductors depending on their structure. Selective opening of the more curved and therefore more chemically reactive "end caps" produces SWCNT with open ends (Fig. **2**).

Preparation of carbon nanotubes usually yields an assembly of nanotubes of different diameters inside one another, which are termed multiple wall carbon nanotubes (MWCNT). The higher curvature of fullerenes accounts for their higher reactivity than graphene, for instance, toward cycloaddition. Calculations by the B3LYP potential implemented in the GAMESS program revealed that the addition of one to six carbenes to a C_{60} fullerene increases electron emission from the molecule without a substantial change of the HOMO-LUMO gap [32]. Functionalization of C_{60} with differently substituted pyrrolidines by [2+3] cycloaddition from glycine derivatives allows for tuning of the energy and location of HOMO [33]. This leads to the increased conductivity ($-NH_2$ substituent) and electron emission ($-NO_2$ substituent) while all pyrrolidine derivatives are predicted to be more soluble in water, and their semiconductor properties are transformed to the n-type [33]. Another way of increasing electron emission from C_{60} is its functionalization by either [2+2] cycloaddition of 2,5-dioxabicyclo[4.2.0]octa-1(8),6-diene, [4+2] addition of 2,3-dimethylene-1,4-dioxane [34], or [4+2] cycloaddition of 2,3-dimethyl-1,3-butadiene [35]. The electron emission increases even more with the number of reacted 2,3-dimethyl-1,3-butadiene molecules [35]. Functionalization of C_{60} with malonate enables its binding with uranyl due to chelating with the carboxyl groups, which is claimed to help with nuclear waste management [36]. However, it is unclear what is the advantage of C_{60} as a malonate carrier for this application.

It was predicted that depending on their diameter and length, SWCNTs are able to adsorb an Ag atom placed inside the tube. Functionalization of the SWCNT edges with either -OH (less effective) or carboxy- (more effective) functional groups enables much stronger binding with Ag replacing the hydrogen atom [37]. Chemical adsorption of Cl or F atoms by the walls of zigzag semiconductor SWCNT reduces the bandgap, while for the metallic armchair SWCNT, it separates the doubly degenerate states crossing the Fermi level. An additional energy level emerged in all modified systems, and their electronic properties, such as metallic or semiconductor behavior, have been substantially altered [38]. Doping of Stone-Wales defective SWCNT with Si was

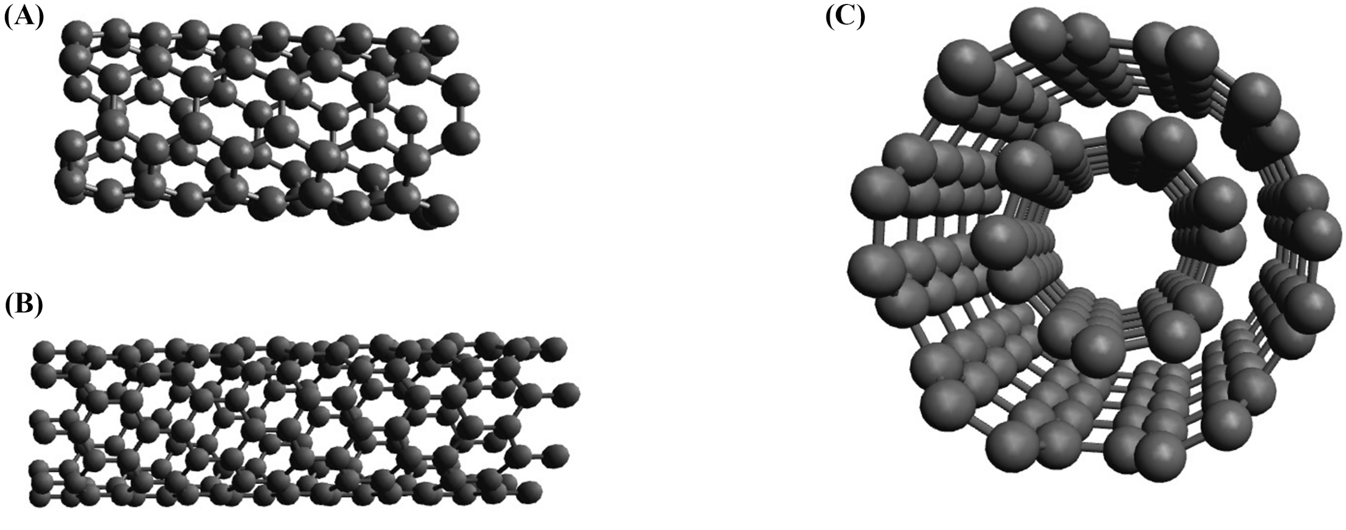

Fig. (2). Structure of a single-wall carbon nanotube (SWCNT). **A**. Metallic armchair (4,4) SWCNT. **B**. Semiconducting zigzag (8,0) SWCNT. **C**. Multiwall carbon nanotube (MWCNT). (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

explored as a potential way to modify the electronic properties of SWCNT [39]. The sidewalls of SWCNT are also predicted to adsorb glycine. The energy of adsorption can be substantially increased by the functionalization of the sidewall with a carboxy-, aldehyde-, or -OH - group [40]. Functionalization of the edge carbon with a variety of electron-donating and electron-withdrawing substituents ($-CH_2NO_2$, $-CH_2CN$, $-CH_2Ph$, $-CH_3$, $-CH_2NH_2$) led to an increase in the HOMO/LUMO energy gap of SWCNT. For electron-withdrawing substituents, LUMO, HOMO, and Fermi levels were shifted to lower energies. Therefore, this type of functionalization may lead to an increment change of the electron emission [41]. Unfortunately, in the calculations, the substituent was simply attached to the edge carbon without removal of the capping hydrogen, which does not model well an actual material. Binding of SWCNTs edge-functionalized with 6-aminohexylamide to Ag^+ decreases the bandgap due to the charge transfer, which stabilizes the complex and increases the electrical conductivity of the material [42].

2.3. Functionalized other Carbons

The common nanodiamonds of 4 nm size are too large for the DFT calculations, which prompted the use of the Molecular Mechanics (MM) geometry optimization of the sp^3-carbon core followed by DFT calculations on a carbon cluster of interest. Two types of functionalities were modeled: carbonyl group by capping of a truncated carbon and carboxy group as a substituent of capping hydrogen [43]. It was predicted that in a vacuum, the carbonyl functionality promoted graphitization, and the carboxy group prefers the edges of the nanocrystal *versus* its corners [43]. Three years later, in 2014, a set of similar structures functionalized by hydrogenation, fluorination, chlorination, oxidation, nitrogenation, and carboxylation was computed by the quantum chemistry methods [44]. The LUMO-HOMO gap was found to be sensitive to the type of functionalization, while fluorination increased the stability of the whole nanoparticle [44]. In 2018, a detailed DFT study explored a range of triangularly or hexagonally shaped graphene flakes of various sizes (graphene quantum dots, GQD) with the edges functionalized with amino-, nitro-, cyano-, isopropyl-, or aldehyde groups in the zigzag or armchair fashion [45]. The energy gap can be tuned through edge functionalization. Depending on the position and mutual positions of attached groups, the total dipole moment can be increased, decreased, or completely eliminated [45]. The group has found that the energy gap significantly decreases when using cluster passivation with oxygen for triangular and hexagonal graphene quantum dots with armchair termination, but the zigzag terminated triangular graphene quantum dots need passivation with fluorine, which is more electronegative than oxygen.

3. FUNCTIONALIZATION OF CARBONS

3.1. Functionalization of Graphene

In 2010, two experimental groups reported functionalization of graphenes by 1,3-dipolar cycloadditions of azomethine ylides generated in situ from an N-glycine derivative and paraformaldehyde [46] or from N-methyl-glycine and 3,4-dihydroxybenzaldehyde [47]. In both reactions, a 1,3-dipole is generated after decarboxylation of the intermediate 4 (Fig. **3**) and is assumed to add to a C=C double bond on a face side of the sp^2-carbon plane of graphene (Fig. **4**). Next year, the energy of the 1,3-dipolar addition of azomethine or carbonyl ylide dipoles to the center, edges, and corners of a series of graphene flakes (Fig. **5**). was explored by the DFT method [48]. It was found that corners and especially edges of the graphene flakes are much more reactive than center because of lesser distortion of the planar geometry of the flake. It was concluded that the experimentally observed 1,3-dipolar functionalization of graphene proceeds, in fact, by the edges as opposed to the center of the graphene flake [48].

Calculations of both the reaction energy and activation barriers for 1,3-dipolar addition and addition of 1,3-butadiene to coronenes (models of graphene) were consistent with the low reactivity of an internal C=C double bond of a flat polyaromatic system [49]. Contrary to 1,3-dipoles, a series of substituted carbenes were predicted to be able to add to the center of a graphene flake [15]. The addition of the next molecule of carbene was more favorable than the addition of the existing one and enabled the tuning of the material's bandgap. Similar to 1,3-dipolar addition, the edges of graphene are more reactive than its inner bonds toward carbenes. However, the accumulation of the added carbenes to the edges did not substantially affect the bandgap [15]. Both the site selectivity of carbene addition and its influence on the bandgap are consistent with the stronger interference

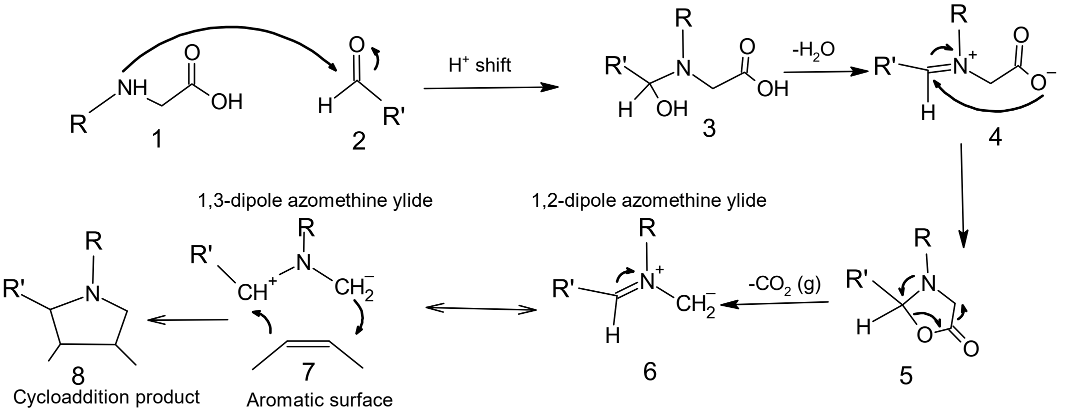

Fig. (3). Formation and 1,3-dipolar addition of an azomethine dipole.

of the added carbene with the electronic structure and geometry of graphene. For the calculations of the energy of intermediates and transition states for the HF-catalyzed fluorination with F_2, coronene was also employed as a model of graphene [50]. Similar to the addition of carbenes, fluorination of an inner C=C double bond seems to be feasible and is likely to produce a mixture of 1,2- and 1,4-products of addition. In both cases, the energies of transition states for the addition of the first and second fluorine atoms are comparable [50].

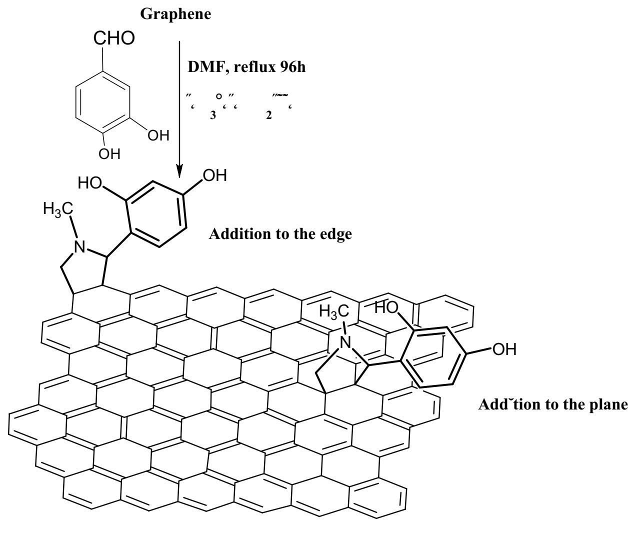

Fig. (4). Products of 1,3-dipolar addition of an azomethine dipole to graphene.

Fabrication of van der Waals heterojunction is a very effective way to improve the electronic and optoelectronic properties of carbonaceous materials. Graphene has dangling free bonds which can form van der Waals heterojunctions with many other 2D materials. Tan *et al.* investigated the heterojunction between graphene and a 2D Bi_2O_2Se crystal for its performance in photodetectors and field-effect transistors and have shown appropriateness of the hybrid materials for this type of device [51].

3.2. Functionalization of Fullerenes

Although fluorination of graphene is predicted to occur both in 1,2- and 1,4-fashion, the curvature of SWCNT makes the addition more regioselective [50]. A (7,7) armchair SWCNT was treated by the ONIOM method, where a curved coronene patch was treated at a higher level of theory than the rest of the system. Contrary to graphene, all identified transition states led to the 1,4-axial product of addition as a consequence of the curvature [50]. However, HF-catalyzed migration of fluorine atoms is possible, leading to 1,2-adducts [50]. Fluorination is an example of the covalent functionalization of SWCNT sidewalls. The 3D structure of SWCNT allows for other functionalization modes, such as functionalization of edge carbons, non-covalent π-π functionalization, and inclusion of guest molecules inside the tube, covered in a comprehensive review [52].

The electron-deficient nature of fullerenes allows for their direct amination with amines. The relationship between reactivity and curvature was explored for the amination of C_{50}, C_{60}, and capped and open armchair (5,5) and zigzag (10,0) SWCNT by methylamine [53]. It was found that carbons at the sites with higher curvature have higher reactivity, such as pentagon-pentagon fusions on C_{50}, the 7-5-5-7 defect on the sidewall of a nanotube, junction of two nanotubes, the end caps, and defect sites [53]. In general, the defect sites in SWCNT are much more reactive and may be introduced to the structure intentionally, for instance, by oxidation [52].

Similar to graphene, a reported 1,3-dipolar addition of azomethine ylides to SWCNT is proposed to occur at the sidewall locations [54]. However, according to the ONIOM model computations of cycloaddition of three dipoles (azomethine ylide, fulminic acid, and methylene nitrone) and 1,3-butadiene to C_{60} and SWCNT, only the 1,3-dipolar cycloadditions of azomethine ylide and fulminic acid to (5,5) SWCNT are exothermic. The rest of the cycloaddition reactions are unfavorable. It was also found that the [6,6] bond of C_{60} is the preferred addition site for all dipoles and butadiene [54]. Therefore, the reported dipolar addition [55] may or may not proceed exclusively at the SWCNT walls. The dipolar addition to fullerenes is proposed for building nanovectors for drug delivery. Thus, an azomethine dipole generated from isoniazid-derivatized glycine can thermodynamically add to both C_{60} and SWCNT. The predicted energies of solvation suggest better solubility in water for isoniazid-derivatized fullerenes [54]. The 1,3-dipolar addition of C_{60} with additional dipoles (nitriloxide and azide) was predicted to be feasible as well [56].

Another study was focused on the sequential cycloaddition of one to six molecules of 2,3-dimethyl-1,3-butadiene to C_{60} [35]. The reaction was found to be regioselective with the preference of addition to the B_{66} bond of C_{60}. The energy of the reaction is decreased with each next molecule of added 2,3-dimethyl-1,2-butadiene [35]. Carbene also adds selectively to the B_{66} bond of C_{60} based on the analysis of the interaction between the SOMO orbital of the carbene and LUMO of C_{60}. Similar to the addition of a diene, the reaction energy is decreased with each next molecule of the added carbene [32]. Due to its inability to adopt an s-cis conformation, C_{60} acts as a dienophile even with the electron-deficient 1,2-benzoquinone in inverse electron-demand Diels-Alder cycloaddition [57]. This group also found that electron-withdrawing substituents in 1,2-benzoquinone favor the reaction according to their electron-withdrawing activity.

One of the first methods of SWCNT functionalization was the Tour's arylation by the decomposition of diazonium salts [58].

The computations are consistent that interaction between SWCNT and aryl radicals is feasible, depending on the tube diameter, chirality, and the number of already added aryl groups [59]. The aryl groups interact with metallic SWCNTs that are significantly stronger than with semiconducting SWCNTs. The aryl radicals interacting with (8,0) SWCNT prefer the pair arrangement, which is consistent with the free radical character of the material with the odd number of added aryl radicals. Further, SWCNTs functional-

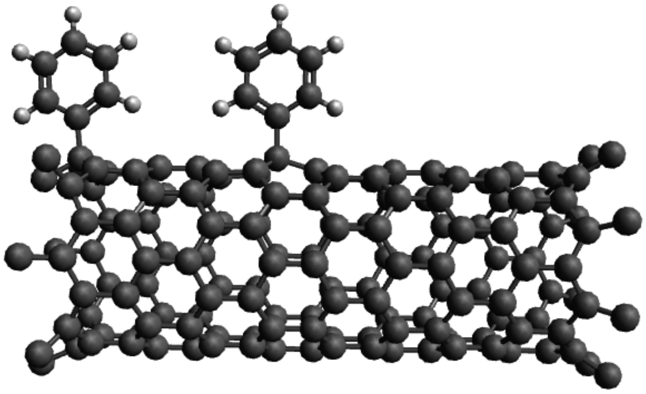

Fig. (5). SWCNT functionalized with aryl radicals. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

ized with an odd number of aryl groups have a smaller bandgap and a higher conductivity than their counterparts with an even number of aryl groups [59]. This work provides a pathway for SWCNT applications in chemical sensors, electronics, and other nanoscale materials. Generation of the aryl radical from a variety of electrophilic reagents would be enabled by placing a negative charge on an SWCNT. In a joint theoretical and experimental study, it was found that at low K:C ratios (<1:200), adsorption of a potassium atom is always preferred on metallic SWCNT *versus* semiconducting ones independently of the tube diameter [60].

Non-covalent interaction plays an important role in the development of composite materials as well as simple, fast, and clean procedures for functionalization. For the extended π-electron systems such as ones present in fullerenes, the effect of π-π stacking is expected to play a major role in the non-covalent functionalization. A computational study conducted side-by-side with the experiment explored the interaction of SWCNT with a polymer containing pyrene groups. For the synthesized and well-characterized complex, the adsorption energy *via* π-π stacking interaction was calculated at the M06-2X/6-31G(d) level of theory after eliminating the basis set superposition errors and was found to be -23.55 kcal/mol [61]. The noncovalent adsorption of 4,4'-methylene diphenyl diisocyanate and toluene-2,4-diisocyanate (TDI) on (6,0) SWCNT) was studied using GGA (PBE) functional including dispersion energy correction for the proper description of van der Waals interactions. It was found that both benzene rings and isocyanate groups substantially participate in the energy of adsorption [62]. If the functionalization relied on the interaction between SWCNT and the benzene rings only, this method could be useful for the simple functionalization of SWCNT with reactive isocyanate groups.

Due to the variable energy bands, unique geometry, and possibility of chirality, SWCNTs are very efficient materials for solar cells, light-emitting diodes, and especially in field-effect transistors. Their performance can be improved by tuning their conductivity and energy bands by functionalization with fullerenes and thus strengthening performance in real-life devices [63].

3.3. Functionalization of Other Carbons

While the bulk of diamond is made of a chemically inert core of sp^3 carbons, the "dangling" bonds on the surface are very reactive, and if left uncapped, form strained C=C double bonds capable of cycloaddition (Fig. **6**).

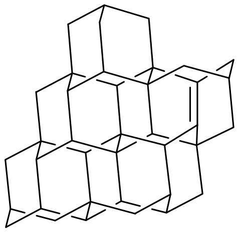

Fig. (6). Fragment of a nanodiamond structure.

A possibility to functionalize the diamond surface by cycloaddition of 1,3-butadiene was explored by computing reaction energies and activation barriers for both [2+2] and [4+2] additions [64]. The lower activation barrier and low product energy for the [4+2] reaction predict that the [4+2] product will be the dominant surface product. A [2+2] reaction is possible. This agrees with experimental evidence that dienes form the [4+2] cycloaddition product [65, 66] while alkenes form the [2+2] product [67].

Doping of carbon quantum dots that can have graphene, diamond, or other structures, is a very efficient way to introduce new energy states. Yaswenth *et al.* investigated the density of states and work function of nitrogen-phosphorus co-doped carbon quantum dots by the first principle theory [68]. They revealed that co-doping carbon quantum dots with nitrogen and phosphorus facilitates the transfer of electrons toward the photocatalytic activity site, which results in the improved photocatalytic activity of the quantum dot-base device. According to Matta *et al*., carbon quantum dots functionalized by -OH and -COOH groups enhance their ability to transport holes in perovskite solar cells [69]. By using the density functional theory, they identified the functionalized hexagonal carbon quantum dots as suitable materials for hole transport in perovskite solar cells.

Adjizian *et al.* applied the DFT method to elucidate the role of sulfur in the production of graphite by the procedure of graphitization. Their calculation suggests that sulfur can form cross-links with defect sides and that the zigzag and armchair edges of graphite are more favorable for cross-linking, which results in more stable graphene edges [70].

4. FURTHER FUNCTIONALIZATION OF FUNCTIONALIZED CARBONS

Once functionalized, a carbonaceous material may increase or decrease its affinity to further functionalization by the same modifier or be enabled for a different type of functionalization. Thus, the introduction of each 1,3-butadiene molecule to C_{60} reduces the energy of cycloaddition with the next molecule of 1,3-butadiene [35]. A similar trend is predicted for the addition of carbene to C_{60} [32]. For 1,3-dipolar addition, the reactivity of C_{60} toward the dipole depends on its type. While the addition of each molecule of azomethine decreases the reactivity of the particle toward the next molecule, the addition of nitriloxides or azides has the opposite effect [56]. The reactivity trend of SWCNTs with aryl radicals fluctuates depending on the number of added aryl groups. The addition of an odd number of aryl groups significantly increases reactivity toward the next group because of the free radical nature of both the modified SWCNT and the incoming aryl radical [59]. Replacement of one atom of carbon in C_{24} with boron and hydrogenation or alkylation of the adjacent carbon activates the system toward polymerization [71].

Presence of carboxy-, aldehyde-, or -OH - groups on the sidewall of an SWCNT significantly increases the energy of adsorption of glycine, which opens the path for the further functionalization of SWCNT with polar molecules [40]. Another study explored how the introduction of new carboxy groups to the SWCNT edges is affected by the existing edge carboxy groups [72]. It was found that the existing edge carboxy groups favor the introduction of more carboxy groups. The energy of carboxylation increases nearly linearly with the number of the edge carboxy groups. The replacement of hydrogen at the edge of a zigzag SWCNT with a carboxy group is more exothermic than for armchair SWCNT, which indicates that zigzag SWCNT are more prone to carboxylation than their armchair counterparts. Further, up to nine carboxy groups can be introduced to one end of a zigzag SWCNT. However, one hydrogen must remain unsubstituted at the end of an armchair SWCNT because of crowding and rim deformation [65]. As expected, functionalization of the edges SWCNTs with 6-aminohexylamide increases their binding to Ag^+ in the gas phase due to the affinity of amines to silver, which is helpful in the design of nanoscale metal ion sensors. The study identified two active sites for interaction with Ag^+: nitrogen of the amino group and oxygen of the carbonyl group [42]. Charging of SWCNTs by their intercalation with potassium atoms [73] increases their reactivity with diazonium cations, which finally leads to arylation. Increasing the K to SWCNT ratio to the sub-stoichiometric leads to the introduction of -OH groups due to oxidation of the negatively charged sites and hydrogen atoms due to their protonation [74].

CONCLUSION

The increasing computing power and discovery of the DFT method have met the demand for theoretical assistance in the design of numerous carbonaceous building blocks for modern nanotechnology. The computational methods are especially critical for predicting electronic properties of materials such as the bandgap, conductivity, optical and photoelectronic properties, solubility, adsorptivity, the potential for catalysis, sensing, imaging, and biomedical applications. At this moment, most computational papers are purely theoretical with a few joint theoretical-experimental studies. They cover a wide range of modification techniques such as doping, functionalization by covalent or non-covalent coupling, and the introduction of defects and electrical charges. The site selectivity of modification, especially with regard to functionalization of defects, is given consideration when it comes to the chemistry of SWCNT. We expect that in the future, this work to be expanded to the area of functionalization of defects in graphene. Functionalization of multiwall carbon nanotubes (MWCNT) and carbon quantum dots is still awaiting computational research, which is understandable considering the structural complexity and diversity of these objects. MWCNTs seem to be completely left out of the field. However, the functionalization of Si, Ge, and Sn quantum dots has already drawn the attention of computational chemists [75]. There are still very few computational works addressing the re-functionalization of carbonaceous materials where their modification enables or alters further functionalization. Keeping in mind that the introduction of defects can be considered as a type of functionalization, re-functionalization of carbonaceous materials seems to be a point of growth in this area of computational research.

CONSENT FOR PUBLICATION

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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REFERENCES

[1] Curl, R.; Kroto, H.W.; Smalley, R.E. Nobel prize in chemistry for 1996. *S. AFR. J. CHEM-S-AFR T,* **1997**, *50*, 102-105.

[2] Dresselhaus, M.S.; Araujo, P.T. Perspectives on the 2010 Nobel Prize in physics for graphene. *ACS Nano,* **2010**, *4*(11), 6297-6302. http://dx.doi.org/10.1021/nn1029789 PMID: 21090813

[3] Chen, K.; Wang, Q.; Niu, Z.; Chen, J. Graphene-based materials for flexible energy storage devices. *J. Energy Chem.,* **2018**, (27), 12-24. http://dx.doi.org/10.1016/j.jechem.2017.08.015

[4] Wu, Z.; Wang, Y.; Liu, X.; Lv, C.; Li, Y.; Wei, D.; Liu, Z. Carbon-nanomaterial-based flexible batteries for wearable electronics. *Adv. Mater.,* **2019**, *31*(9), e1800716. http://dx.doi.org/10.1002/adma.201800716 PMID: 30680813

[5] Dai, Ch.; Sun, G.; Hu, L.; Xiao, Y.; Zhang, Zh.; Qu, L. Recent progress in graphene-based electrodes for flexible batteries. *Infomat,* **2020**, *2*, 529-526. http://dx.doi.org/10.1002/inf2.12039

[6] Tian, W.; Li, W.; Yu, W.; Liu, X. A review on lattice defects in graphene: types. generation, effects and regulation. *Micromachines (Basel),* **2017**, *8*(5) http://dx.doi.org/10.3390/mi8050163

[7] Song, S.; Zhao, H.; Zheng, X.; Zhang, H.; Liu, Y.; Wang, Y.; Han, B. A density functional theory study of the role of functionalized graphene particles as effective additives in power cable insulation. *R. Soc. Open Sci.,* **2018**, *5*(2), 170772. http://dx.doi.org/10.1098/rsos.170772 PMID: 29515821

[8] Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.,* **1996**, *77*(18), 3865-3868. http://dx.doi.org/10.1103/PhysRevLett.77.3865 PMID: 10062328

[9] Kresse, G.; Furthmüller, J.J.C. m. s. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Elsevier,* **1996**, *6*(1), 15-50.

[10] Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B Condens. Matter,* **1996**, *54*(16), 11169-11186. http://dx.doi.org/10.1103/PhysRevB.54.11169 PMID: 9984901

[11] Saha, B.; Bhattacharyya, P.K. Adsorption of amino acids on boron and/or nitrogen doped functionalized graphene: A Density Functional Study. *Comput. Theor. Chem.,* **2016**, *1086*, 45-51. http://dx.doi.org/10.1016/j.comptc.2016.04.017

[12] Scalmani, G.; Frisch, M.J. Comment on A smooth, nonsingular, and faithful discretization scheme for polarizable continuum models: The switching/gaussian approach. *J. Chem. Phys.,* **2011**, *134*(11), 117101. http://dx.doi.org/10.1063/1.3567489 PMID: 21428670

[13] Sánchez‐Portal, D.; Ordejon, P.; Artacho, E.; Soler, J.M.J.I.c. Density‐functional method for very large systems with LCAO basis sets. *Int. J. Quantum Chem.,* **1997**, *65*(5), 453-461. http://dx.doi.org/10.1002/(SICI)1097-461X(1997)65:5<453::AID-QUA9>3.0.CO;2-V

[14] Sharma, J.D.; Ahluwalia, P.; Kumar, N. In: *Study of electron density of states of nano structured functionalized graphene within DFT calculations*; AIP Conference Proceedings AIP, **2011**, pp. 321-322. http://dx.doi.org/10.1063/1.3653739

[15] Zan, W. Chemical functionalization of graphene by carbene cycloaddition: A density functional theory study. *Appl. Surf. Sci.,* **2014**, *311*, 377-383. http://dx.doi.org/10.1016/j.apsusc.2014.05.071

[16] Giannozzi, P. Baroni, S. Bonini, N.Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I.J.J. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Condens. Matter Phys.,* **2009**, *21*(39), 395502. http://dx.doi.org/10.1088/0953-8984/21/39/395502

[17] Wood, B.C.; Bhide, S.Y.; Dutta, D.; Kandagal, V.S.; Pathak, A.D.; Punnathanam, S.N.; Ayappa, K.G.; Narasimhan, S. Methane and carbon dioxide adsorption on edge-functionalized graphene: A comparative DFT study. *J. Chem. Phys.,* **2012**, *137*(5), 054702. http://dx.doi.org/10.1063/1.4736568 PMID: 22894366

[18] Anithaa, V.; Vijayakumar, S. Effect of side chain edge functionalization in pristine and defected graphene-DFT study. *Comput. Theor. Chem.,* **2018**, *1135*, 34-47. http://dx.doi.org/10.1016/j.comptc.2018.05.006

[19] Dobrota, A.S.; Pašti, I.A.; Mentus, S.V.; Johansson, B.; Skorodumova, N.V. Functionalized graphene for sodium battery applications: The DFT insights. *Electrochim. Acta,* **2017**, *250*, 185-195. http://dx.doi.org/10.1016/j.electacta.2017.07.186

[20] Rad, A.S. Al-doped graphene as a new nanostructure adsorbent for some halomethane compounds: DFT calculations. *Surf. Sci.,* **2016**, *645*, 6-12. http://dx.doi.org/10.1016/j.susc.2015.10.036

[21] Liu, Z.; Zhang, Y.; Wang, B.; Cheng, H.; Cheng, X.; Huang, Z. DFT study on Al-doped defective graphene towards adsorption of elemental mercury. *Appl. Surf. Sci.,* **2018**, *427*, 547-553. http://dx.doi.org/10.1016/j.apsusc.2017.07.293

[22] López-Corral, I.; Germán, E.a.; Juan, A.; Volpe, M.A.; Brizuela, G.P. DFT study of hydrogen adsorption on palladium decorated graphene. *J. Phys. Chem. C,* **2011**, *115*(10), 4315-4323. http://dx.doi.org/10.1021/jp110067w

[23] Zhang, H.P.; Luo, X.G.; Song, H.T.; Lin, X.Y.; Lu, X.; Tang, Y. DFT study of adsorption and dissociation behavior of H_2S on Fe-doped graphene. *Appl. Surf. Sci.,* **2014**, *317*, 511-516. http://dx.doi.org/10.1016/j.apsusc.2014.08.141

[24] Luo, H.; Cai, J.; Tao, X.; Tan, M.J.A.s. Adsorption and dissociation of H_2S on Mo (10 0) surface by first-principles study. *Appl. Surf.,* **2014**, *292*, 328-335. http://dx.doi.org/10.1016/j.apsusc.2013.11.140

[25] Luque, G.; Rojas, M.; Rivas, G.; Leiva, E. The origin of the catalysis of hydrogen peroxide reduction by functionalized graphene surfaces: a density functional theory study. *Electrochim. Acta,* **2010**, *56*(1), 523-530. http://dx.doi.org/10.1016/j.electacta.2010.09.016

[26] Esrafili, M.D.; Vessally, E. N_2O + CO reaction over single Ga or Ge atom embedded graphene: A DFT study. *Surf. Sci.,* **2018**, *667*, 105-111. http://dx.doi.org/10.1016/j.susc.2017.10.001

[27] Li, L.; Reich, S.; Robertson, J. Defect energies of graphite: density-functional calculations. *Phys. Rev. B Condens. Matter Mater. Phys.,* **2005**, *72*(18), 184109. http://dx.doi.org/10.1103/PhysRevB.72.184109

[28] Susi, T.; Kaukonen, M.; Havu, P.; Ljungberg, M.P.; Ayala, P.; Kauppinen, E.I. Core level binding energies of functionalized and defective graphene. *Beilstein J. Nanotechnol.,* **2014**, *5*(1), 121-132. http://dx.doi.org/10.3762/bjnano.5.12 PMID: 24605278

[29] Mortensen, J.J.; Hansen, L.B.; Jacobsen, K.W. *Phys. Rev. B Condens. Matter Mater. Phys.,* **2005**, *71*, 035109. http://dx.doi.org/10.1103/PhysRevB.71.035109

[30] Guo, X.; Huang, S. Tuning nitrogen reduction reaction activity *via* controllable Fe magnetic moment: a computational study of single Fe atom supported on defective graphene. *Electrochim. Acta,* **2018**, *284*, 392-399. http://dx.doi.org/10.1016/j.electacta.2018.07.168

[31] Yang, S.; Li, S.; Tang, S.; Shen, D.; Dong, W.; Sun, W. Adsorption, intercalation and diffusion of Na on defective bilayer graphene: a computational study. *Surf. Sci.,* **2017**, *658*, 31-37. http://dx.doi.org/10.1016/j.susc.2017.01.004

[32] Baei, M.T.; Peyghan, A.A.; Bagheri, Z. Electronic, energetic, and geometric properties of methylene-functionalized C_{60}. *J. Cluster Sci.,* **2013**, *24*(3), 669-678. http://dx.doi.org/10.1007/s10876-013-0563-6

[33] Peyghan, A.A.; Soleymanabadi, H.; Moradi, M. Structural and electronic properties of pyrrolidine-functionalized [60] fullerenes. *J. Phys. Chem. Solids,* **2013**, *74*(11), 1594-1598. http://dx.doi.org/10.1016/j.jpcs.2013.05.030

[34] Peyghan, A.A.; Noei, M. DFT study on [4+ 2] and [2+ 2] cycloadditions to [60] fullerene. *Chem. Zvesti,* **2014**, *68*(3), 409-416. http://dx.doi.org/10.2478/s11696-013-0448-z

[35] Beheshtian, J.; Peyghan, A.A.; Bagheri, Z. Functionalization of [60] fullerene with butadienes: A DFT study. *Appl. Surf. Sci.,* **2012**, *258*(22), 8980-8984. http://dx.doi.org/10.1016/j.apsusc.2012.05.134

[36] Jena, N.K.; Sundararajan, M.; Ghosh, S.K. On the interaction of uranyl with functionalized fullerenes: A DFT investigation. *RSC Advances,* **2012**, *2*(7), 2994-2999. http://dx.doi.org/10.1039/c2ra01143c

[37] Zhang, Z.; Hao, Y.; Wang, L.; Dong, M.; Hou, W.; Han, P.; Liu, X.; Xu, B. DFT studies of ag-loading intrinsic and functionalized single-walled carbon nanotubes. *Chin. J. Chem.,* **2012**, *30*(1), 121-126. http://dx.doi.org/10.1002/cjoc.201180449

[38] Pan, H.; Feng, Y.P.; Lin, J. Ab initio study of F-and Cl-functionalized single wall carbon nanotubes. *J. Condens. Matter Phys.,* **2006**, *18*(22), 5175. http://dx.doi.org/10.1088/0953-8984/18/22/017

[39] Anafcheh, M.; Ghafouri, R. Silicon doping of defect sites in Stone–Wales defective carbon nanotubes: A density functional theory study. *Superlattices Microstruct.,* **2013**, *60*, 1-9. http://dx.doi.org/10.1016/j.spmi.2013.04.014

[40] Ganji, M.; Bakhshandeh, A. Functionalized single-walled carbon nanotubes interacting with glycine amino acid: DFT study. *Physica B,* **2011**, *406*(23), 4453-4459. http://dx.doi.org/10.1016/j.physb.2011.09.006

[41] Beheshtian, J.; Peyghan, A.A.; Bagheri, Z. Carbon nanotube functionalization with carboxylic derivatives: a DFT study. *J. Mol. Model.,* **2013**, *19*(1), 391-396. http://dx.doi.org/10.1007/s00894-012-1569-y PMID: 22936348

[42] Mehdizadeh, K.; Giahi, M. A DFT study on N-6-amino-hexylamide functionalized single-walled carbon nanotubes in interaction with silver ion in a gaseous environment. *J. Nanostructure Chem.,* **2019**, *9*(1), 39-51. http://dx.doi.org/10.1007/s40097-019-0296-7

[43] Datta, A.; Kirca, M.; Fu, Y.; To, A.C. Surface structure and properties of functionalized nanodiamonds: A first-principles study. *Nanotechnology,* **2011**, *22*(6), 065706. http://dx.doi.org/10.1088/0957-4484/22/6/065706 PMID: 21212485

[44] Brown, N.; Hod, O. Controlling the electronic properties of nanodiamonds *via* surface chemical functionalization: A DFT study. *J. Phys. Chem. C,* **2014**, *118*(10), 5530-5537. http://dx.doi.org/10.1021/jp409236t

[45] Abdelsalam, H.; Elhaes, H.; Ibrahim, M.A. Tuning electronic properties in graphene quantum dots by chemical functionalization:

Density functional theory calculations. *Chem. Phys. Lett.,* **2018**, *695*, 138-148.
http://dx.doi.org/10.1016/j.cplett.2018.02.015

[46] Quintana, M.; Spyrou, K.; Grzelczak, M.; Browne, W.R.; Rudolf, P.; Prato, M. Functionalization of graphene *via* 1,3-dipolar cycloaddition. *ACS Nano.,* **2010**, *4*(6), 3527-3533.
http://dx.doi.org/10.1021/nn100883p PMID: 20503982

[47] Georgakilas, V.; Bourlinos, A.B.; Zboril, R.; Steriotis, T.A.; Dallas, P.; Stubos, A.K.; Trapalis, C. Organic functionalisation of graphenes. *Chem. Commun. (Camb.),* **2010**, *46*(10), 1766-1768.
http://dx.doi.org/10.1039/b922081j PMID: 20177643

[48] Cao, Y.; Houk, K. Computational assessment of 1,3-dipolar cycloadditions to graphene. *J. Mater. Chem.,* **2011**, *21*(5), 1503-1508.
http://dx.doi.org/10.1039/C0JM02422H

[49] Osuna, S.; Houk, K.N. Cycloaddition reactions of butadiene and 1,3-dipoles to curved arenes, fullerenes, and nanotubes: Theoretical evaluation of the role of distortion energies on activation barriers. *Chemistry,* **2009**, *15*(47), 13219-13231.
http://dx.doi.org/10.1002/chem.200901761 PMID: 19876972

[50] Osuna, S.; Torrent-Sucarrat, M.; Sola, M.; Geerlings, P.; Ewels, C.P.; Lier, G.V. Reaction mechanisms for graphene and carbon nanotube fluorination. *J. Phys. Chem. C,* **2010**, *114*(8), 3340-3345.
http://dx.doi.org/10.1021/jp908887n

[51] Tan, C.; Xu, S.; Tan, Z.; Sun, L.; Wu, J.; Li, T.; Peng, H. Exploitation of Bi2O2Se/graphene van der Waals heterojunction for creating efficient photodetectors and short‐channel field‐effect transistors. *InfoMat,* **2019**, *1*, 390-395.
http://dx.doi.org/10.1002/inf2.12025

[52] Rümmeli, M.H.; Ayala, P.; Pichler, T. Carbon nanotubes and related structures: Production and formation; Wiley Online Library, **2010**, pp. 1-22.

[53] Lin, T.; Zhang, W-D.; Huang, J.; He, C. A DFT study of the amination of fullerenes and carbon nanotubes: reactivity and curvature. *J. Phys. Chem. B,* **2005**, *109*(28), 13755-13760.
http://dx.doi.org/10.1021/jp051022g PMID: 16852723

[54] Gallo, M.; Favila, A.; Glossman-Mitnik, D. DFT studies of functionalized carbon nanotubes and fullerenes as nanovectors for drug delivery of antitubercular compounds. *Chem. Phys. Lett.,* **2007**, *447*(1-3), 105-109.
http://dx.doi.org/10.1016/j.cplett.2007.08.098

[55] Georgakilas, V.; Tagmatarchis, N.; Pantarotto, D.; Bianco, A.; Briand, J-P.; Prato, M. Amino acid functionalization of water soluble carbon nanotubes. *ChemComm.,* **2002**, *24*, 3050-3051.

[56] Anafcheh, M.; Ghafouri, R. Mono-and multiply-functionalized fullerene derivatives through 1,3-dipolar cycloadditions: A DFT study. *Physica. E.,* **2014**, *56*, 351-356.
http://dx.doi.org/10.1016/j.physe.2013.10.013

[57] Hazrati, M.K.; Hadipour, N.L. A DFT study on the functionalization of C60 fullerene with 1, 2-benzoquinone. *Comput. Theor. Chem.,* **2016**, *1098*, 63-69.
http://dx.doi.org/10.1016/j.comptc.2016.11.007

[58] Dyke, Ch.A.; Tour, J.M. Covalent functionalization of single-walled carbon nanotubes for materials applications. *J. Phys. Chem. A,* **2004**, *108*(51), 11151-11159.
http://dx.doi.org/10.1021/jp046274g

[59] Zhao, J-x.; Ding, Y-h. Chemical functionalization of single-walled carbon nanotubes (SWNTs) by aryl groups: A density functional theory study. *J. Phys. Chem. C,* **2008**, *112*(34), 13141-13149.
http://dx.doi.org/10.1021/jp8030607

[60] Gebhardt, J.; Bosch, S.; Hof, F.; Hauke, F.; Hirsch, A.; Görling, A.J.J.M.C.C. Selective reduction of SWCNTs – concepts and insights. *J. Mater. Chem. C Mater. Opt. Electron. Devices,* **2017**, *5*(16), 3937-3947.
http://dx.doi.org/10.1039/C5TC01407G

[61] Özgen, P.S.O.; Durmaz, H.; Parlak, C.; Alver, Ö.; Bağlayan, Ö. Non-covalent functionalization of single walled carbon nanotubes with pyrene pendant polyester: A DFT supported study. *J. Mol. Struct.,* **2020**, *1209*, 127943.
http://dx.doi.org/10.1016/j.molstruc.2020.127943

[62] Goclon, J.; Kozlowska, M.; Rodziewicz, P. Noncovalent functionalization of single-walled carbon nanotubes by aromatic diisocyanate molecules: A computational study. *Chem. Phys. Lett.,* **2014**, *598*, 10-16.
http://dx.doi.org/10.1016/j.cplett.2014.02.042

[63] Delacou, C.; Jeon, I.; Otsuka, K.; Inoue, T.; Anisimov, A.; Fujii, T.; Kauppinen, E.I.; Maruyama, S.; Matsuo, Y. Investigation of charge interaction between fullerene derivatives and single‐walled carbon nanotubes. *InfoMat.,* **2019**, *1*, 559-570.
http://dx.doi.org/10.1002/inf2.12045

[64] Fitzgerald, D.R.; Doren, D.J. Functionalization of diamond (100) by cycloaddition of butadiene: First-principles theory. *J. Am. Chem. Soc.,* **2000**, *122*(49), 12334-12339.
http://dx.doi.org/10.1021/ja002023j

[65] Wang, G.T.; Bent, S.F.; Russell, J.N.; Butler, J.E.; D'Evelyn, M.P.J.J.A.C.S. Functionalization of diamond (100) by Diels− Alder chemistry. *J. Am. Chem. Soc.,* **2000**, *122*(4), 744-745.
http://dx.doi.org/10.1021/ja993024i

[66] Hossain, M.Z.; Aruga, T.; Takagi, N.; Tsuno, T.; Fujimori, N.; Ando, T.; Nishijima, M.J.J.J.A.P. Diels-Alder reaction on the clean diamond (100) 2× 1 surface. *Jpn. J. Appl. Phys.,* **1999**, *38*(12B), L1496.
http://dx.doi.org/10.1143/JJAP.38.L1496

[67] Hovis, J.; Coulter, S.; Hamers, R.; D'Evelyn, M.; Russell, J.; Butler, J.J.J.A.C.S. Cycloaddition chemistry at surfaces: Reaction of alkenes with the diamond (001)-2× 1 surface. *J. Am. Chem. Soc*., **2000**, *122*(4), 732-733.63.

[68] Hurst Jr, M.O.; Hurst Sr, M.O.; Fortenberry, R.C. Boron-doped c24 fullerenes for alkyl functionalization or potential polymerization. *ACS Omega,* **2018**, *3*(1), 1001-1006.

[69] Yashwanth, H.; Rondiya, S.R.; Dzade, N.Y.; Dhole, S.; Phase, D.; Hareesh, K.J.V. Enhanced photocatalytic activity of N, P, co-doped carbon quantum dots: An insight from experimental and computational approach. *Elsevier,* **2020**, *180*, 109589.

[70] Kasi Matta, S.; Zhang, C.; O'Mullane, A.P.; Du, A. Density functional theory investigation of carbon dots as hole-transport material in perovskite solar cells. *ChemPhysChem,* **2018**, *19*(22), 3018-3023.
http://dx.doi.org/10.1002/cphc.201800822 PMID: 30252194

[71] Adjizian, J.-J.; Latham, C.; Öberg, S.; Briddon, P.; Heggie, M.J.C. DFT study of the chemistry of sulfur in graphite, including interactions with defects, edges and folds. *Elsevier,* **2013**, *62*, 256-262.

[72] Hurst, M.O., Jr; Hurst, M.O., Sr; Fortenberry, R.C. Boron-Doped C_{24} fullerenes for Alkyl functionalization or potential polymerization. *ACS Omega,* **2018**, *3*(1), 991-996.
http://dx.doi.org/10.1021/acsomega.7b01767 PMID: 31457943

[73] Chełmecka, E.; Pasterny, K.; Kupka, T.; Stobiński, L. DFT studies of COOH tip-functionalized zigzag and armchair single wall carbon nanotubes. *J. Mol. Model.,* **2012**, *18*(5), 2241-2246.
http://dx.doi.org/10.1007/s00894-011-1242-x PMID: 21965032

[74] Schirowski, M.; Tyborski, C.; Maultzsch, J.; Hauke, F.; Hirsch, A.; Goclon, J. Reductive diazotation of carbon nanotubes: An experimental and theoretical selectivity study. *Chem. Sci. (Camb.),* **2018**, *10*(3), 706-717.
http://dx.doi.org/10.1039/C8SC03737J PMID: 30746106

[75] Walker, B.; Hendy, S.; Tilley, R. *In Density functional studies of surface functionalization in semiconductor quantum dots*; AIP Conference Proceedings AIP, **2009**, pp. 98-101.
http://dx.doi.org/10.1063/1.3203257