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Mapping the molecular electrostatic potential of carbon nanotubes

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ABSTRACT

Because of the emerging applications of carbon nanotubes, the understanding of surface properties is still a hot topic of research. This work is conducted to map the electrostatic potential ESP of carbon nanotubes (CNT). CNT and their ZnO and CuO decorated structures are subjected to DFT calculations at B3LYP/6-31g*. Through the ESP the possible sites of electrophilic or nucleophilic attack can easily be identified. So that, ESP expresses the ability of the given CNT to interact with its surrounding through its surface by forming bonding and/or forming surface interactions and could be a perfect index for reactivity of CNT. The mapping contours of the studied structures and the total surface indicated that the distribution of charges and the electrostatic contour is affected by decoration which dedicated the decorated CNT for many applications.

Keywords: *CNT; CNT/ZnO; CNT/CuO; B3LYP/6-31g*; ESP.*

1. INTRODUCTION

Since the discovery of CNT early on 1991 [1], it is a topic of extensive work according to their unique chemical, physical and mechanical properties. As a result of their surface properties, CNTs are tried as an adsorbent, for the removal of pollutants from the aquatic environment. So that, many researchers studied the adsorption of heavy metals as well as other organic compounds [2-6]. For further applications of CNTs researchers find out that treating the surface is an important step for a so-called functionalization of CNTs. Some researchers pointed out that, such functionality could be achieved by oxidation treatment [7-8].

Early on1999, it is stated that among the works actually devoted to the possible applications CNTs are to incorporate CNTs with metals [9-10].

It is stated that CNTs have unique hollow and layered structure with a high specific surface area, besides excellent electrical conductivity, high chemical stabilities; this in turn leads to ion transport gaps. According to these advantages, CNTs could be good carriers for metal oxides. This finding paves the way toward introducing metal oxides into CNTs. It is stated that CNTs/metal oxides composites are an effective strategy to achieve improved capacitance, cyclability and rate performance [11-14].

Understanding the effect of functionalization upon CNTs is important to direct the application of functional CNTs. Molecular modeling calculations especially those depending on Density Functional Theory DFT and Ab Initio methods are widely applied to investigate physical, chemical structural and electronic properties of many systems and molecules [15-18]. These models could be utilized recently to understand the behavior and structures of CNTs as well as their nanocomposites in a different area of research [19-23].

Modeling molecular electrostatic potential with a higher level of theory is an important step to understand the behavior and properties of a given surface especially for those could be applied in biological interactions. It is stated that the electrostatic potential is among the main factors determining the interfacial band offsets and charged defect energetic [24-27]. This reflects in determining the sites for reactivity of a given compound.

The present work is devoted to study CNT as well as ZnO; CuO decorated CNT at B3LYP/6-31g* level of theory.

2. EXPERIMENTAL SECTION

2.1. Calculations details. In the present study, we build a model molecule for CNT and decorated CNT with 3ZnO-H, 3OZn-H, 5CuO-H, 5OCu-H, 5CuO-5OCu-H and 10CuO-10OCu-H. All the studied model molecules are subjected to calculations with GAUSSIAN09 [28] program at Spectroscopy Department, National Research Centre, Egypt. All the model molecules are subjected to optimization at B3LYP/6-31g* [29-31]. Molecular electrostatic potential and total surface are also calculated at the same level of theory.

3. RESULTS SECTION

3.1. Building Model Molecules. Model molecules representing CNT is indicated as in figure 1. CNT is supposed to be decorated with 3ZnO-H, 3OZn-H, 5CuO-H, 5OCu-H, 5CuO-5OCu-H and 10CuO-10OCu-H which are calculated at B3LYP/6-31g*.

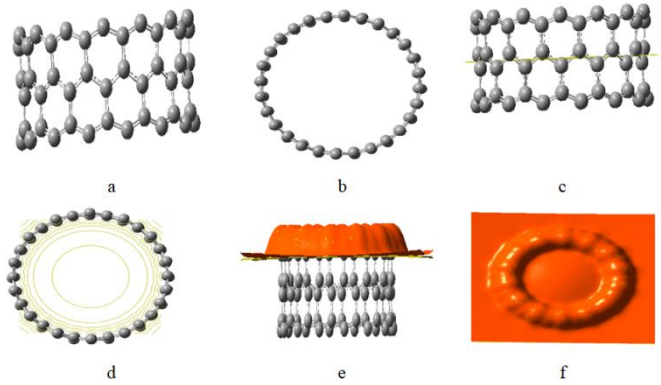

Figure 1. B3LYP/6-31g* optimized structure for a, b- CNT, c, d- ESP of CNT, e, f- total surface of CNT.

To describe the studied models, CNT surface is supposed to interact with 3ZnO-H, 3OZn-H, 5CuO-H, 5OCu-H, 5CuO-5OCu-H and 10CuO-10OCu-H respectively through the complex state as indicated in figures 2 up to 7.

For each model, the structure is optimized then the molecular electrostatic potential is mapped as contour then as total surface area.

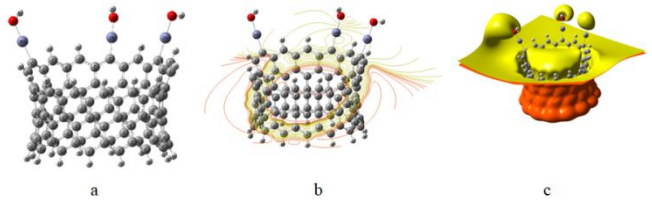

Figure 2. B3LYP/6-31g* optimized structure for a- CNT decorated with 3ZnO-H; b- ESP of the same structure, c-total surface for the same structure.

3.2. Molecular Electrostatic Potential Surface Analysis. To describe the molecular electrostatic potential it is important first to understand what is meant by ESP at a certain point then gather this to remaining surface. At a given point in a given surface ESP could be physically described as the energy required to bring a single positive charge from infinity to that point. According to this simple definition of mapping, the points constituting the surface of CNT is going to describe wheather the surface of CNT which contains such points that could further interact. Another important point is how to activate the surface of CNT to be able for interaction. ESP in this sense could be described as a key index of the molecular reactivity of CNT.

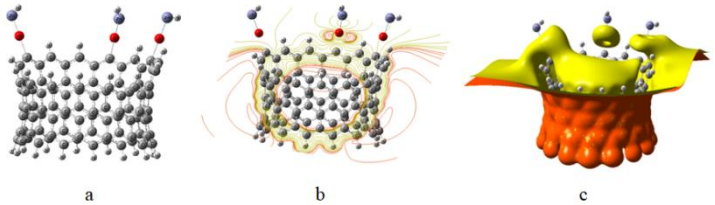

Figure 3. B3LYP/6-31g* optimized structure for a- CNT decorated with 3OZn-H; b- ESP of the same structure, c-total surface for the same structure.

Figure 1-a and b presents the optimized CNT structure from two different views. Figure 1-c and 1-d present the ESP contour for both views of CNT. The contour from outside CNT is in the middle while localized inside the CNT as indicated in figure 1-d. ESP is uniformly distributed at the middle wall and inside the CNT. The surface is localized on the top of the CNT.

It is clear that the ESP contour of CNT indicates that there is a uniform distribution of ESP. Also, the surface is uniformly up the CNT.

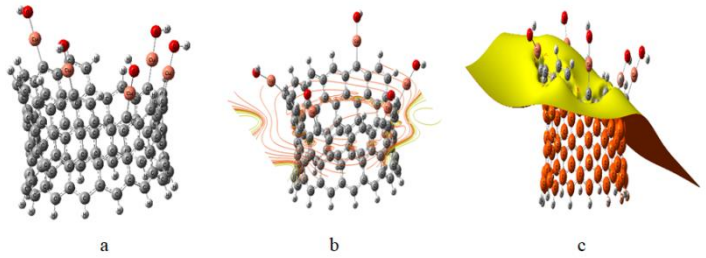

Figure 4. B3LYP/3-21g * optimized structure for a- CNT decorated with 5CuO-H; b- ESP of the same structure, c-total surface for the same structure.

This could explain the need for changing the surface properties of CNT by decoration.

Figure 2 presents the effect of decoration with 3ZnO-H, in which Zn is interacting with the CNT surface then able to further interact with structure throughout forming a hydrogen bond. Figure 3 presents the same interaction between CNT and Zinc oxide with the difference that ZnO is interacting with CNT through oxygen not through Zn.

The uniform contour of CNT is changed as a result of decoration with ZnO.

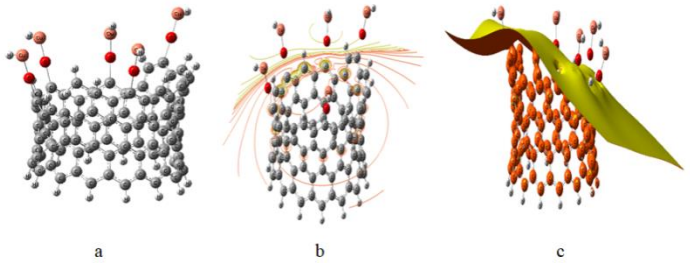

Figure 5. B3LYP/6-31g* optimized structure for a-CNT decorated with 5OCu-H; b- ESP of the same structure, c-total surface for the same structure.

Regarding figure 4 whereas CNT is interacting with 5CuO-H once through Cu and then through oxygen as indicated in figure 5. Figures 6, 7 present the CNT decorated with 5CuO-5OCu-H and 10CuO-10OCu-H respectively. The behavior is the same that the contour of CNT lost its uniform distribution of ESP. More precise description of the molecular electrostatic potential could be discussed as in the following points. As stated earlier that, the contour of ESP is describing the surface of CNT as well as decorated CNT by mapping the sites for both electrophilic and nucleophilic attacks [32]. It describes the charge distributions for the studied CNT and decorated CNT throughout colors. Mapping the colors could be the indication for the site, such that ongoing from negative to positive the colors are going from red to blue. This means that the negativity is following the color scheme as in

the following potential color order red< orange < yellow < green < blue which is already described before [33-34]. The decoration is going to change the ESP which enhances the surface ability to interact and dedicating decorated CNT for many applications. Regarding the color scheme of the previous ESP one can conclude that hydrogen bonding coming as a result of the electrophilic active regions are found as a result of decoration. Decorated CNT could be further carried out structures containing hydrogen which dedicate the decorated CNT for a wide range of application starting from sensors, energy storage materials up to drug delivery systems.

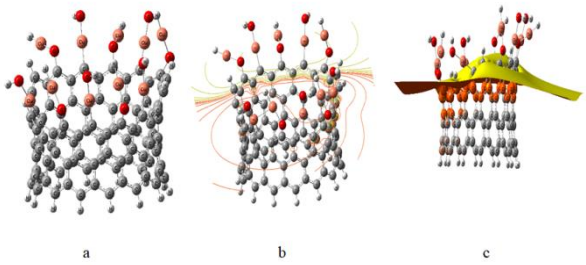

Figure 6. B3LYP/6-31g* optimized structure for a- decorated CNT decorated with CNT-5CuO-5OCu-H; b- ESP of the same structure, c-total surface for the same structure.

The surface itself is showing different morphology as one compares between the surfaces of CNT before and after metal oxide decoration.

On the other hand DFT at B3LYP/6-31g * is a suitable level of theory for studying CNT as well as their metal oxides decorated structures.

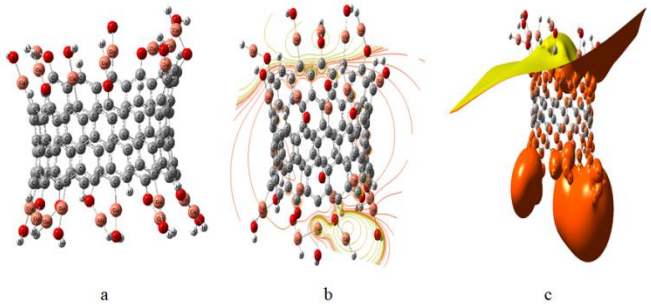

Figure 7. B3LYP /6-31g* optimized structure for a- CNT decorated with 10CuO-10OCu-H; b- ESP of the same structure, c-total surface for the same structure.

Regarding the surface of decorated CNT in comparison with that of CNT indicates an increase in the surface with the existence of deformation. Correlating this with that of ESP indicates that decoration increases the functionality of CNT.

4. CONCLUSIONS

DFT at B3LYP/6-31g* level is suitable model to map the ESP of CNT and ZnO and CuO decorated CNT. ESP indicated the possible sites for electrophilic or nucleophilic attack. Decoration is changing the ESP through enhancing the surface ability for interaction. Hydrogen bonding as a result of the electrophilic active regions is found after decoration. So that, decorated CNT could be dedicate for sensing applications, energy storage materials also as drug delivery systems.

Comparing between the surface of decorated CNT with that of CNT indicates surface increment with deformation, which in turn increases the functionality of decorated CNT.

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