

# *Graphene-based composites materials for fuel cell: Computational study*

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**Abstract**—In order to make the effective use of renewable energy, it is important to develop high-performance, low-cost and environmental friendly energy conversion systems like fuel cell. Currently, Pt catalyst electrodes are the most common electrodes used in fuel cell systems. However, traditional Pt catalyst electrodes have many disadvantages. Graphene-based composites materials can be an interesting non-noble catalyst for oxygen reduction reaction (ORR) that occurs in the cathode of fuel cell. A computational study was carried out to investigate the electronic structure properties of grapheme and graphene-based composites. The catalytic effect of graphene, and graphene-based composites in acidic environment was studied by using density functional theory (DFT). The simulations demonstrate that the oxygen reduction reaction (ORR) occurs only in nitrogen doped graphene. From this study, the ORR on nitrogen doped graphene is a four-electron transformation pathway. The nitrogen doped graphene can be a catalyst for the ORR cathode of fuel cells in acidic environment, and can be an excellent alternative for platinum.

**Keywords**- Graphene, fuel cell, oxygen reduction reaction (ORR), density functional theory (DFT), non noble electrocatalyst, doped graphene

## I. INTRODUCTION

Due to the rapid industrial development and growing human population, along with the increase energy demand, the global energy consumption has been accelerating at a high rate. To prevent problems caused by energy exhaustion, the need for renewable energy sources has attracted tremendous attention around the world. In order to make the effective use of renewable energy, it is important to develop high-performance, low-cost and environmental friendly energy conversion and storage systems. Fuel cells are the systems required for promising electrochemical energy conversion [1].

A fuel cell is a device, which directly converts chemical energy into electric energy. With no pollution, it has a high conversion rate and a wide application use, which will make it one of the energy sources in future human society. Currently, Pt catalyst electrodes are the most common electrodes used in fuel cell systems. However, traditional Pt catalyst electrodes have many disadvantages, which affect its industrialization. Therefore, the selection and preparation of high-performance electrodes is an important research project in fuel cells. Pt-

based fuel cells are expensive and will suffer from CO poisoning [2,3], which prohibits the fuel cells from large-scale applications. Therefore, the development of a Pt-free oxygen reduction reaction (ORR) catalyst remains challenging and many efforts have been devoted in this direction.

Recently, doped nanostructured carbon materials, have been considered as an alternative catalysts for the ORR due to their high catalytic activity and durability toward ORR [4-5]. Doping constitutes a powerful route to tailor the electronic properties of graphene. In this paper, the DFT method was used to study the electronic structure properties of graphene and M doped graphene (M: single atom of bore, aluminum, silicon, phosphor, nitrogen). The catalytic effect of graphene, and M doped graphene (M: single atom of bore, aluminum, silicon, phosphor, nitrogen) in acidic environment was investigated by using DFT. Finally, the mechanism of ORR on nitrogen doped graphene was illustrated.

## II. SIMULATION METHOD AND MODELS

B3LYP hybrid density functional theory of Gaussian 09 [6] was employed with a basis set of 6-31G(d,p) [7]. Considering the breaking and forming of the chemical bond, unstrict polarization setting was used in the calculation. Doped graphene sheets were built by substitution of carbon atom by other single atom M. Six types of atoms were used: Bore, aluminum, silicon, phosphor and nitrogen. For comparison, graphene sheets with the same configuration but no doping were also constructed. Carbon atoms on the edge of the graphene are terminated by hydrogen atoms. As first stage M doped graphene structure were optimized. In the second stage of this study, the graphene and doped graphene were used as catalyst in ORR. Because the reaction occur in acidic media, the ORR processes were simulated by placing the molecule OOH near the graphene or doped graphene with the OOH molecular plane parallel to the sheet plane, with a distance of 3.0 Å away from the sheet [8].

### III. RESULTS AND DISCUSSION

Optimized structure and charge distribution of: graphene sheet C<sub>24</sub>H<sub>12</sub> and doped graphene sheets C<sub>23</sub>BH<sub>12</sub>, C<sub>23</sub>AlH<sub>12</sub>, C<sub>23</sub>SiH<sub>12</sub>, C<sub>23</sub>PH<sub>12</sub>, and C<sub>23</sub>NH<sub>12</sub> are shown in Figure 1

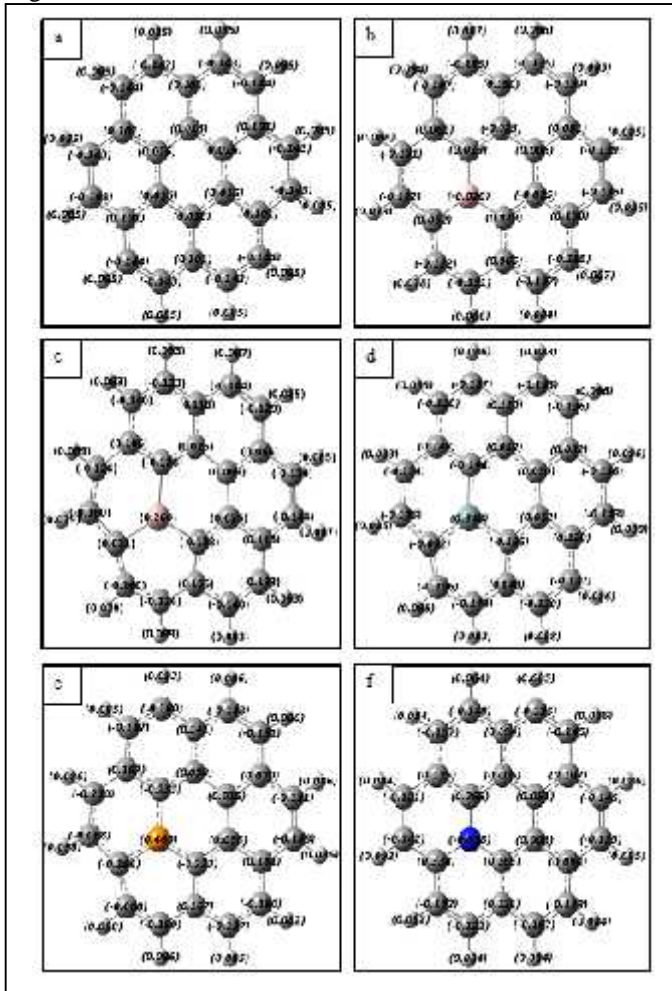
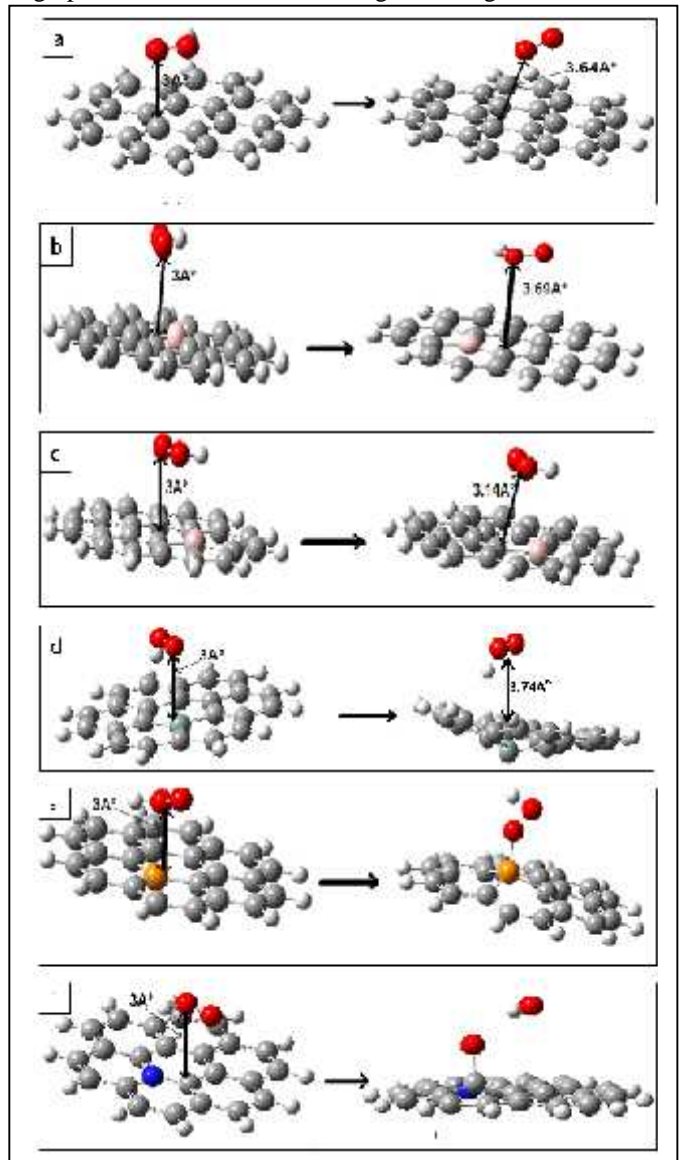


Figure 1. Optimized structure and charge distribution of: (a) C<sub>24</sub>H<sub>12</sub>, (b) C<sub>23</sub>BH<sub>12</sub>, (c) C<sub>23</sub>AlH<sub>12</sub>, (d) C<sub>23</sub>SiH<sub>12</sub>, (e) C<sub>23</sub>PH<sub>12</sub>, (f) C<sub>23</sub>NH<sub>12</sub>. The number is the charge value of each atom

From graphene sheet in the Figure 1.a, the atoms charges of central hexagon graphene sheet are zero and the distance between the carbon atoms is 1.42 Å. In the bore doped graphene (Figure 1b), the decrease of the charge of the carbon atom bonded with bore was observed, the structure of this sheet is similar to that of graphene sheet. The charge of aluminum atom is very high in aluminum doped graphene, however the charges of carbon atoms are very low (Figure 1c). Doping

graphene sheet by silicon atom leads to the decrease of the charge of all carbon atoms but the silicon atom show a high charge (Figure 1d). The phosphor doped graphene sheet is characterized by high positive charge for phosphor atom and low charge for carbon atoms bonded with phosphor atom (Figure 1e). In the nitrogen doped graphene, the value of the charge of the carbon atom bonded with the nitrogen atom is high and the structure of the nitrogen doped graphene sheet is very similar to graphene sheet (Figure 1f). Substitutional doping of bore, aluminum, silicon, phosphor and nitrogen in graphene sheet leads to the change in charge distribution and



structure. This doping can also change other properties like: spin density, vibration modes, total energy and HUMO-LUMO energy (these results will be presented and discussed in the full version of the paper).

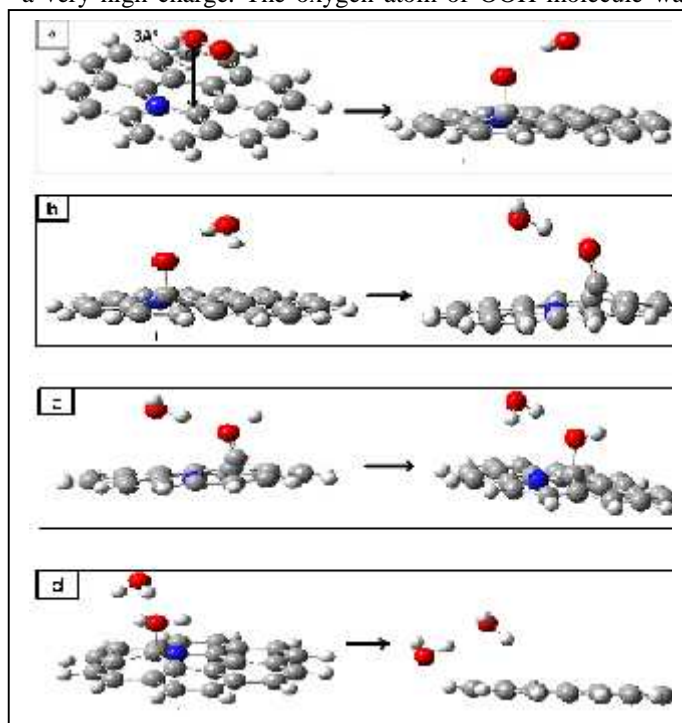
Figure 2. Simulation of beginning of ORR reaction on: (a) C24H12, (b) C23BH12, (c) C23AlH12, (d) C23SiH12, (e) C23PH12, (f) C23NH12. In the left side before optimization, in the right side after optimization.

The optimized structure of graphene and doped graphene were used as catalysts for ORR in order to replace platinum in fuel cells. The ORR processes were simulated beginning with the first electron transmission, in which process the intermediate molecule OOH was already formed. This is possible because in acidic environment, O<sub>2</sub> can adsorb an H<sup>+</sup> to form H<sup>+</sup>-O-O, because the whole system is charge neutral [8]. OOH<sup>+</sup> could be simplified to OOH, and subsequent adsorbed H<sup>+</sup> could be taken as H by considering the ionization potentials. And there are no net charges on the graphene and doped graphene. The simulation of ORR processes were started by placing the molecule OOH near the graphene or doped graphene with the OOH molecular plane parallel to the sheet plane, with a distance of 3.0 Å away from the sheet [8]. The first step of simulation of ORR processes for graphene and doped boron, aluminum, silicon, phosphor, nitrogen graphene is presented in Figure 2. After the optimization of the system composed of graphene sheet and OOH molecule, no interaction was observed between this molecule and the sheet (Figure 3a). The distance between the OOH molecule and the graphene sheet was increased from 3.0 Å before the optimization to 3.64 Å after the optimization. We can conclude that it was repulsion between graphene sheet and the molecule OOH. The graphene can't be a catalyst for the ORR.

The distance between OOH molecule and boron doped graphene after optimization was increased to 3.69 Å and no interaction was observed (Figure 2b). No interaction was observed in the case of aluminum doped graphene and the increase of the distance between the OOH molecule and the sheet was recorded (Figure 2c). After the optimization the silicon doped graphene sheet was deformed and the repulsion between the OOH molecule and the sheet was observed (Figure 2d). After the optimization of the system composed of the phosphor doped graphene and OOH molecule, we have observed the break of the bond O-O in the molecule OOH, the deformation of the molecule of phosphor out of the plan of the sheet and the formation of bond between oxygen atom and phosphor atom (Figure 2e). This interaction can't be the beginning of ORR. The graphene and the doped graphene with atom of boron, aluminum, silicon, and phosphor didn't show catalytic effect for the ORR. The nitrogen doped graphene show an interaction between the OOH molecule and the sheet, this interaction can be a beginning of the ORR process (Figure 2f). Further results and more interpretations will be presented in the full paper version to explain why some doped graphene show a catalytic effect for the ORR and other don't show any effect.

In Figure 3, we present the different steps of ORR in nitrogen doped graphene. This Figure shows the structural change of nitrogen doped graphene and adsorbed molecules for each reaction step, at which an H atom was sequentially introduced into the system.

In the first step of the reaction, the carbon atom bonded with nitrogen was deformed out of plan sheet, this carbon has a very high charge. The oxygen atom of OOH molecule was



detached after the break of the bond O-O in the OOH molecule. The free molecule of oxygen was bonded to the carbon atom bonded with the nitrogen atom. The distance between the carbon and oxygen atoms was reduced to 1.47 Å from 3.0 Å, further confirming the formation of a chemical bond between oxygen and graphene. This is an important step for nitrogen doped graphene to have catalytic activities because adsorption and formation of chemical bond is necessary for the following reactions. In the second step, we introduce another H to the system. The H atom was placed near to the oxygen atom of the molecule OH. After the optimization of the system, the H atom was bonded to OH molecule to constitute the first H<sub>2</sub>O molecule. The oxygen atom bonded to the graphene forms another bond with the same carbon atom. In the third step, when another H is introduced into the system and after the

Figure 3. Simulation of different steps of ORR on nitrogen doped graphene (a) first step, (b) second step, (c) third step, (d) fourth step. In the left side before optimization, in the right side after optimization.

optimization the break of one of the double bonds between oxygen and graphene and the formation of bond between this oxygen atom and the added H atom. Also the distance between H<sub>2</sub>O molecule and the graphene sheet was increased, which means the repulsion between the H<sub>2</sub>O molecule and nitrogen doped graphene. Another H atom was added to the system in the fourth step, the optimization was performed. At the end of this step, the break of the bond of oxygen atom and the carbon atom, the formation of bond between H atom to OH molecule to constitute a second H<sub>2</sub>O molecule were observed.

Also, the distance between the first H<sub>2</sub>O molecule and the nitrogen doped graphene was increased. After the two water molecules drift away from the nitrogen doped graphene, the nitrogen doped graphene recovers to its initial state. Here, the ORR process finishes and the nitrogen doped graphene is ready for the next catalytic reaction cycle. At each step, the adsorption energy for these molecules on the nitrogen graphene was calculated (results not shown). In each step of transformation, the energy becomes more negative, driving the system to a more stable state. From this study, the ORR on nitrogen doped graphene is a four-electron transformation pathway, which is consistent with the experimental results [5].

#### CONCLUSION

The DFT method was used to study the graphene-based composites materials, these materials were built by the substitutional doping of boron, aluminum, silicon, phosphorus, nitrogen in graphene. This doping changes the electronic properties of graphene sheet. The DFT method was also used to study the mechanism of ORR on the graphene and doped graphene cathode of fuel cells in acidic environment. The graphene and the doped graphene with atom of boron, aluminum, silicon, and phosphorus didn't show catalytic effect for the ORR. The nitrogen doped graphene can be a catalyst for the ORR cathode of fuel cells in acidic environment. From this study, the ORR on nitrogen doped graphene is a four-electron transformation pathway.

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