

# DFT Study of Electric Capacity for Composites Building by Phosphomolybdic Acid with Nitrogen Doped Graphene

Caihua Zhou (✉ [xbdxzch@126.com](mailto:xbdxzch@126.com))

Xianyang Normal University <https://orcid.org/0000-0003-2342-0342>

Chao Wang

Xianyang Normal University

Guang Fan

Xianyang Normal University

---

## Research Article

**Keywords:** DFT, Composites, PMA, Doped Graphene

**Posted Date:** April 30th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-471427/v1>

**License:**   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

**Version of Record:** A version of this preprint was published at Journal of Inorganic and Organometallic Polymers and Materials on August 6th, 2021. See the published version at <https://doi.org/10.1007/s10904-021-02081-3>.

# DFT Study of Electric Capacity for Composites Building by Phosphomolybdic Acid with Nitrogen-Doped Graphene

Caihua Zhou\*<sup>1</sup> Chao Wang<sup>1</sup> Guang Fan<sup>1</sup>

## Abstract

Three kinds of composites were built by nitrogen-doped grapheme and phosphomolybdic acid. Based on the density functional theory, the combined energies, charge populations, orbital distributions and densities of states (DOS) were calculated. The results show that the short range interaction can be formed between oxygen atom and nitrogen atom, and the charge can be transferred from phosphomolybdic acid to graphene. It is found that the conductive bands (CB) of phosphomolybdic acid move to lower level energy and there are more valence bands (VB) in composites from DOS. It is revealed that composites have the higher electric capacity due to nitrogen-doped graphene can receive more electrons from phosphomolybdic acid.

**Keywords:** DFT; Composites; PMA; Doped Graphene

## Introduction

Phosphomolybdic acid (PMA) is a kind of metal-oxygen cluster. It has the cage structure, can behave properties of electronic donor and electronic capacity. It is very high thermal stability, and it easily dissolve in polar solvent. In the past decade, many people think it is a potential electric capacity material<sup>1-3</sup>. PMA also belong to the heteropoly acid, which has the excellent oxide-reducing ability. Lots of reports also found PMA can react with the carbon nanomaterial, and can produce a perfect electrode material. Especially, graphene as the thinnest material with the large surface and conductive rate, it is almost the significant carbon material to combine with PMA. However, the micro mechanism of composites (PMA combine with carbon nanomaterial) inducing the excellent electric capacity is rare reports. A mainly reason is due to the graphene is be difficultly saluted by polar solvent. So chemical modify of graphene become a popular method to change its dissolvent<sup>4-6</sup>. Some people hope to make the oxide-graphene, some people doped other element into graphene<sup>7-9</sup>. Lots of reports have been revealed that nitrogen doped graphene has great dissolving properties when it composites with PMA<sup>10</sup>. Those experimental data also found that nitrogen atom can provide it's electrons to graphene, and lots of nitrogen atoms will induce deficiency in graphene plane<sup>11-13</sup>. At same time, when nitrogen atoms dope with graphene, nitrogen atoms will lost electrons displaying positive charge, which can form stable chemical bonds with other atoms<sup>14</sup>. Therefore, many papers have especially investigated the types of chemical bond about nitrogen doped into grapheme. Currently, three types of nitrogen-doping micro-modes have been confirmed: (1) A nitrogen atom replaced of a carbon

---

<sup>1</sup> Caihua Zhou xbdxzch@126.com

<sup>1</sup> Department of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang 712000, China

atom in graphene plane. (2) A nitrogen atom connect with two carbon atoms producing a six-member pyridine ring, but a carbon atom lost from another C-N bond and induce the formation of deficiency in graphene plane. (3) A nitrogen atom still connect with two carbon atoms, but it produces a five-member pyrrole ring, also a carbon atom lost from another C-N bond and induce the formation of another deficiency in graphene plane<sup>15-17</sup>. However, how did the phosphomolybdic acid combined with nitrogen-doped graphene according to different mode? Are there different chemical bonds between them? And which factor influences their electric capacity when phosphomolybdic acid combined with the modified graphene. In order to reveal the intrinsic on nitrogen-doped graphene combining with PMA, the above-mentioned three modes were built, and the combined sites, combined energy and combined interactions were investigated in here. The micro-mechanism of increased electric capability is discussed for three kinds of composites.

### Calculated Detail

All of the DFT calculations were performed using plane-wave pseudopotential method, as implemented in CASTEP module in Materials Studio8.0<sup>18</sup>. The general gradient approximation (GGA) with PBE functional<sup>19</sup> and the ultra-soft pseudopotential<sup>20</sup> were used to describe the exchange correlation effects and electron-ion interactions, respectively. The wave functions were expanded into a basis set of plane waves with a kinetic energy cut-off of 500 eV. The self-consistent convergence accuracy was set at  $2.0 \times 10^{-5}$  eV/atom, the convergence criterion for the force between atoms was  $5 \times 10^{-2}$  eV/Å, and the maximum displacement was  $2 \times 10^{-3}$  Å. Based on the optimized structure, the LDA+U approach [22] was utilized for electronic properties investigation. The optimized lattice parameters is that the hexagonal lattice with  $6 \times 6$  graphene unit cell ( $a=14.820$  Å,  $b=14.820$  Å;  $\alpha=\beta=90, \gamma=120$ ) was calculated. As a result, three kinds of composites about nitrogen-doped graphene and PMA were constructed according to a hexagonal cell with periodic boundary conditions of dimensions  $14.82/14.82/25.14$  (x/y/z) Å, in which the interspaces of monolayer graphene and PMA was  $2.0$  Å along the  $z$  direction. The vacuum layer was located above graphene monolayer along  $c$  axis in the super-cell for separating the adjacent unit, and the depth of the vacuum layer was  $20$  Å.

### Discussion and Results

#### Structural optimization and electronic properties of three nitrogen-doped models.

Based on the graphene super-cell, three nitrogen-doped graphene super-cells also were built. In model **A**, a nitrogen atom replaced a carbon atom, and then three C-N bonds were formed. That is, a nitrogen atom is available for three pyridines (Figure 1a). However, due to more carbon atoms maybe lost when graphene was modified, the deficiency could happen in graphene plane. If nitrogen atom combined with carbon atoms, two types of aromatic hydrocarbon ring could be made. Such as, in model **B** (Figure 1b), a nitrogen atom connecting with carbons results in a pyridine, and in model **C** (Figure 1c), a nitrogen atom connecting with carbon atoms forms a pyrrole. In order to build the unity model, two hydrogen atoms was used to saturate two carbon atoms with suspend bonds in

model **B** and **C**. Compare with the enthalpy of graphene, the enthalpy of three nitrogen doped graphene become more negative (Table 1). Thus, the modified process for nitrogen doped into graphene should meet requirement of thermodynamics theory, and the model of three kinds of nitrogen-doped graphene should be reasonable. Based on the optimized structure, the orbital energies and atomic charges of three models also have been calculated. From Table 1, three types of nitrogen-doped graphene has similar HOMO energies, about  $-0.15\text{Ha}$ . But their LUMO energies are obviously different. Among three LUMO energies, model **A** has the highest LUMO energy, and model **B** has the lowest LUMO energy. As a result, for model **A**, there is no deficiency in graphene plane, and the frontier orbital energy gap is bigger than that of model **B** and **C**. Due to the more low energy gap of molecules, the better reaction activity, it can be inferred that the deficiency of graphene can promote the reaction activity of nitrogen-doped graphene.

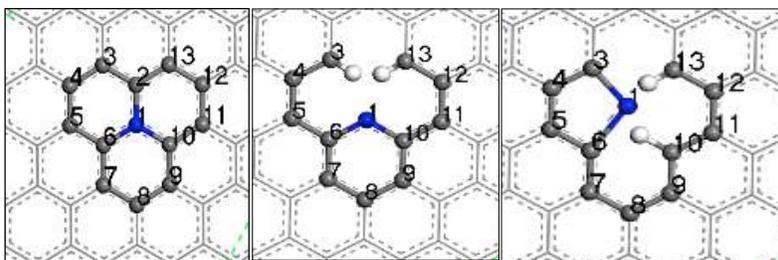


Figure 1 the models of three types nitrogen doped graphene (left **A**, center **B**, right **C**)

Table 1 Frontier orbital energies ( $\epsilon$ ) of all model and binding energy (BE) of three composites

	$\epsilon_{\text{HOMO}}/\text{(Ha)}$	$\epsilon_{\text{LUMO}}/\text{(Ha)}$	$\Delta\epsilon/\text{(Ha)}$	Energy $/\text{(Ha)}$	BE $/\text{(Ha)}$
Model A	-0.14701	-0.09243	0.05458	-2760.8755	
Model B	-0.15514	-0.15371	0.00142	-2723.8403	
Model C	-0.15471	-0.14481	0.00991	-2723.7968	
A+PMA( <b>1</b> )	-0.24302	-0.24012	0.00290	-7562.0191	-1.14
B+PMA( <b>2</b> )	-0.24270	-0.23897	0.00373	-7524.2927	-0.99
C+PMA( <b>3</b> )	-0.22632	-0.22177	0.00454	-7524.9476	-1.11
PMA	-0.32637	-0.32468	0.00169	-4800.4444	
Graphene	-0.258564	-0.258087	0.00047	-2791.23345	

For the nitrogen atoms affect the charge distributions in the graphene, the corresponding atomic charge (NPA) were calculated. From table 2, it can be seen that nitrogen atoms induce the change of atomic charge. For the model **A**, when a nitrogen atom replaces of a carbon atom, the nitrogen atom with high electronegativity shows negative charge. All the carbon atom showed positive charges, and carbon atoms (C(2), C(6)and C(10)) connecting with nitrogen atom show the bigger positive charge than others due to the N–C(2) N–C(6) and N–C(10) bonds have the bigger polarity than C–C bonds. However, for model **B** and model **C**, besides the nitrogen atom, C (3) and C(13) also show negative charge due to the atomic deficiency of model **B** and model **C**. The negative charge of nitrogen is the highest in model **A**, and the lowest negative charge of nitrogen is in model **C**. The C(7), C(8), C(11) and C(12) always remain positive charge in three models, and the highest positive charge can be found in model **C**. From the charge population, it can conclude that the structure of model **C**

induces the bigger molecular polarity. Compare to the model **B**, the structure of model **C** become the more asymmetric, it should be the important reason for the bigger polarity of model **C**.

### The structural optimization and electronic properties of PMA

Phosphomolybdic acid (PMA) is a kind of heteropolyacid, and a unit of PMA includes forty oxygen atoms. That is there are twelve molybdenum atoms, one phosphor atom and three hydrogen atoms in a PMA. The calculated PMA model is shown in Figure 2, and the chemical formula of PMA is  $[\text{PMo}_{12}\text{O}_{40}]\text{H}_3$ . In PMA structure, the center phosphor atoms coordinate with four oxygen atoms, and twelve MoO6 units circle with it. In order to get a natural molecule, three hydrogen atoms were connected to three oxygen atoms. The crystal structure of PMA from CCDC, the cell parameters of PMA are got from CCDC ( $a = 9.9147\text{\AA}$ ,  $b = 9.9147\text{\AA}$ ,  $c = 8.6508\text{\AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ). The general gradient approximation (GGA) with PBE functional and the ultra-soft pseudopotential were used to describe the exchange correlation interactions effects and electron-ion interactions. Based on the optimized crystal structure, the monomer  $[\text{PMo}_{12}\text{O}_{40}]\text{H}_3$  was get (Figure 2), and the orbital energies and charge populations were calculated by B3LYP/6-31G.

Table 2 The Charge Population of All Model

	Model A	Model B	Model C	A+PMA(1)	B+PMA(2)	C+PMA(3)
N (1)	-0.667	-0.515	-0.492	-0.682	-0.310	-0.377
C (2)	0.211			0.300		
C (3)	0.006	-0.307	-0.039	0.041	-0.234	0.021
C (4)	0.016	0.050	0.142	0.075	0.247	-0.213
C (5)	0.006	0.048	-0.039	0.043	-0.045	-0.213
C (6)	0.211	0.142	0.142	0.300	0.095	0.003
C (7)	0.006	0.016	0.056	0.296	0.090	0.034
C (8)	0.016	0.014	0.022	0.081	0.01	0.022
C (9)	0.006	0.016	-0.000	0.029	0.003	0.021
C (10)	0.211	0.142	-0.188	0.032	-0.16	-0.208
C (11)	0.006	0.048	0.061	0.038	0.092	0.037
C (12)	0.016	0.050	0.062	0.081	0.02	0.035
C (13)	0.006	-0.307	-0.188	-0.021	-0.042	-0.208

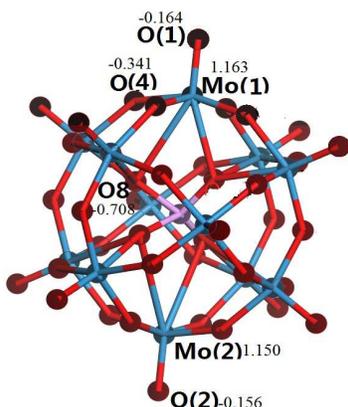


Figure 2 The structure of PMA

The calculated results show that the PMA has very low energy gap, which means that the PMA should have enough reactive activity. The orbital population shows that *p* orbitals of oxygen atoms contribute to HOMO orbital, and *d* orbitals of metal Mo and *p* orbitals of P atoms contribute to the LUMO orbital. From the structure of monomer PMA, three kinds of oxygen atoms were found. It is corresponding with the NPA charge populations of PMA. From figure 2, it can be seen that those oxygen atoms that only connect with one Mo atom have the lowest negative charge, those oxygen atoms that connect with one Mo and one P have the highest negative charge, and the other oxygen atoms that connect with two Mo atoms show a commonly negative charge.

### Structural Optimization and Electronic Properties of Three Types of Composites

In order to investigate the combined interactions of composites, the combined energies of three composites were calculated by DFT. It is hypothesized that the reactants are nitrogen-doped graphene and PMA, and the products are composites. That is, Model (A or B or C) + PMA  $\rightarrow$  Composites.  $\Delta E = E(\text{Com}) - E(\text{Mod}) - E(\text{PMA})$ . And the calculated data was analyzed according to this reaction equation. The combined energies were concluded as shown in Table 2. Three composites have the negative combined energies, that is, model A, B and C of nitrogen-doped graphene can combine with PMA producing stable composites. For Model B and C, the deficiency induces the electrons-rich region of the models, which is beneficial for the electric capacity of the materials. And the calculated charge and orbital population also can explain similar properties. From the charge population of

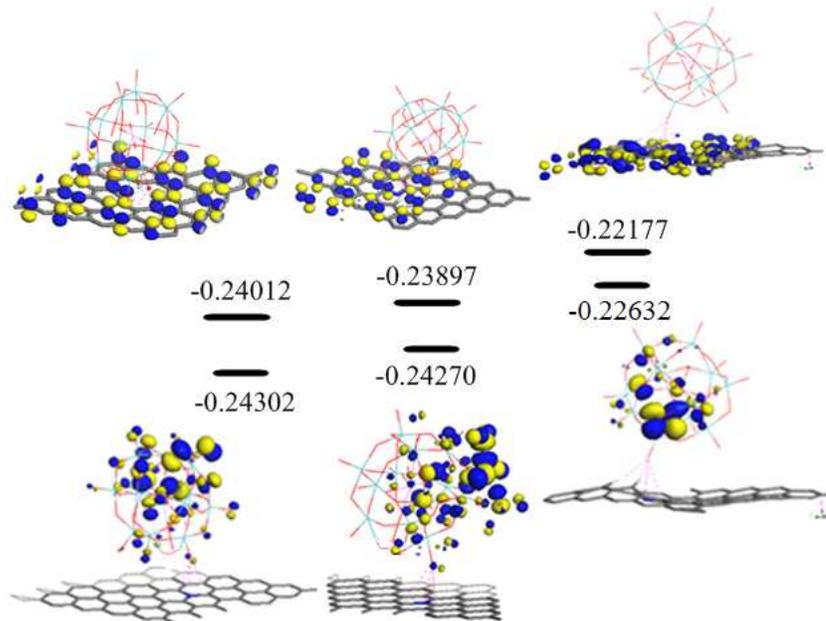


Figure 3 the frontier orbital distribution of three composite3

Table 2, it can see that all those atomic charges become the lower in three kinds of composites than in three models of nitrogen-doped graphene. And the charges of carbons obviously became the lower in composite **2** and **3**. So it is concluded that charges transferred from PAM to nitrogen-doped graphene has occurred in three composites. When we observed the frontier orbitals compositions of three composites in Figure 3, we found that HOMO orbital is mainly from orbitals of PMA. For the LUMO orbital is mainly from nitrogen-doped graphene in three composites. For composite **3**, the energies of HOMO and LUMO become very high and the energy gap is the biggest. It means that composite **3** is the most stable. However, from Figure 3, it is found that the graphene plane was changed, there is a little curled on the plane. That is, the deficiency induces the curled change of plane in composite **3**.

### **The Density of state for three types of composites**

The density of states (DOS) of composites and **PMA** were calculated. Figure 4 have plotted the density of states of bulk **PMA** and composite **1**, **2** and **3**. For bulk **PMA**, the conduction bands (CB) mainly originate from the contribution of  $3d$  orbitals of Mo atoms, and the contributions of valence bands (VB) between  $-1.3$  eV and  $-20$  eV are from  $2p$  orbital of oxygen and P atoms. For lower energy levels ( $-35$  eV to  $-60$  eV), the major contributions are from  $2s$  orbital of oxygen and phosphorus atoms, and there are not energy levels between  $-8$ eV –  $-19$ eV. When nitrogen-doped graphene combines with PMA, their DOS have been changed. From Figure 4, the orbital contributions of CB and VB in composite **1** are similar to that of composite **2**, and the energy levels are found at Fermi point and within  $-8$ eV–  $-19$ eV regions. These continuous energy levels are mainly belonging to the energy levels of graphene. For three composites, Mo atomic  $3d$  orbitals still are the main components of CB, in which the strong electronic coupling can be found between monolayer graphene and the metal Mo. Moreover, for composite **2** and **3**, defective carbon atoms decrease interfacial electrostatic repulsion between **PMA** and graphene, which promote the electrons transfer from Mo atoms to carbon atoms. However, the DOS of composite **3** is different from the composite **1** and **2**. There are still energy levels between  $-8$ eV –  $-19$ eV, but the energy levels are not found at Fermi point. Due to the obvious curl of plane in composite **3**, the Fermi point of graphene was destroyed. Compare to with **PMA**, three composites have the more many VB level, they should have the bigger electrons' capacity.

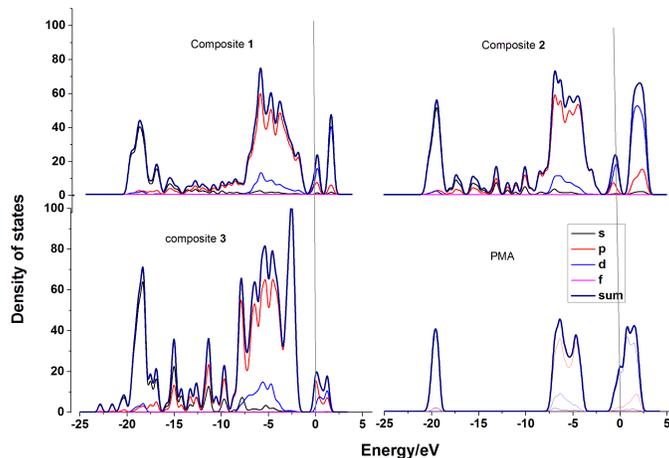


Figure 4 the density of states for three composites and PMA

## Conclusion

Electronic structures and the density of states of bulk PMA and PMA-graphene composites have been investigated using the first-principle method. The calculated results show that doped-nitrogen atoms affect the structures and electron properties of PMA-graphene composites. PMA can combine with nitrogen-doped graphene by oxide-redox reaction, PMA play the donor, nitrogen-doped graphene accepts the electrons from PMA. As a result, three composites have the bigger capacity of electrons than PMA. The specific results is following:

1. For composite **1**, nitrogen atom has light effect on graphene, the Fermi point can be obviously found. The frontier orbital energy gap also has little change. From the atomic charge calculation, the charges transfer was found from PMA to graphene.
2. For composite **2**, nitrogen atom induces the deficiency, also induce the change of electronic structures and atomic charges, and enlarge the frontier orbital energy gap.
3. For composite **3**, there is also deficiency in nitrogen-doped graphene. Due to the formation of pyrrole ring affects the coplanar of graphene, the most obvious change of electronic structures and atomic charge were displayed in composite **3**. It has the biggest combined energy, the biggest energy gap and the curly change of planar structures.

That is, in composite **3**, for deficiency of carbon atom and formation of five ring, the electronic structure is significantly changed, which behaves obvious electronic coupling between carbon and Mo atoms, charges can be efficiently transported from PMA to graphene.

## Acknowledge

This project was supported by the Science Foundation of Shaan'xi Province (No. 2018JM2033), Shaan'xi Provincial Education Department Project (No. 18JK0836), Undergraduate Training Programs for Innovation (No. 201828004) and the Teaching Reform Project (No. 2017Y007).

## Reference

1. Guo, S. X.; Zhang, Y.; Zhang, X.; Easton, C. D.; MacFarlane, D. R.; Zhang, J., Phosphomolybdic Acid-Assisted Growth of Ultrathin Bismuth Nanosheets for Enhanced Electrocatalytic Reduction of CO<sub>2</sub> to Formate. *ChemSusChem* **2019**, *12* (5), 1091-1100.
2. Hatori, M.; Moriya, S.; Fujimori, M.; Kobayashi, S.; Ikota, H.; Shirabe, K.; Yokoo, H.; Kimura, K.; Saio, M., Phosphomolybdic Acid Prevents Nonspecific Nuclear Staining by Picosirius Red but Is Converted to Molybdenum Blue by Blue Light. *J Histochem Cytochem* **2020**, *68* (9), 621-634.
3. Jia, X.; Shen, L.; Yao, M.; Liu, Y.; Yu, W.; Guo, W.; Ruan, S., Highly efficient low-bandgap polymer solar cells with solution-processed and annealing-free phosphomolybdic acid as hole-transport layers. *ACS Appl Mater Interfaces* **2015**, *7* (9), 5367-72.
4. Joucken, F.; Tison, Y.; Le Fevre, P.; Tejada, A.; Taleb-Ibrahimi, A.; Conrad, E.; Repain, V.; Chacon, C.; Bellec, A.; Girard, Y.; Rousset, S.; Ghijsen, J.; Sporcken, R.; Amara, H.; Ducastelle, F.; Lagoute, J., Charge transfer and electronic doping in nitrogen-doped graphene. *Sci Rep* **2015**, *5*, 14564.
5. Kumar, A.; Banerjee, K.; Dvorak, M.; Schulz, F.; Harju, A.; Rinke, P.; Liljeroth, P., Charge-Transfer-Driven Nonplanar Adsorption of F4TCNQ Molecules on Epitaxial Graphene. *ACS Nano* **2017**, *11* (5), 4960-4968.
6. Kwon, S. S.; Shin, J. H.; Choi, J.; Nam, S.; Park, W. I., Defect-Mediated Molecular Interaction and Charge Transfer in Graphene Mesh-Glucose Sensors. *ACS Appl Mater Interfaces* **2017**, *9* (16), 14216-14221.
7. Ferre-Vilaplana, A.; Herrero, E., Charge transfer, bonding conditioning and solvation effect in the activation of the oxygen reduction reaction on unclustered graphitic-nitrogen-doped graphene. *Phys Chem Chem Phys* **2015**, *17* (25), 16238-42.
8. Jiang, D.; Du, X.; Liu, Q.; Hao, N.; Wang, K., MoS<sub>2</sub>/nitrogen doped graphene hydrogels p-n heterojunction: Efficient charge transfer property for highly sensitive and selective photoelectrochemical analysis of chloramphenicol. *Biosens Bioelectron* **2019**, *126*, 463-469.
9. Pei, W.; Zhang, T.; Wang, Y.; Chen, Z.; Umar, A.; Li, H.; Guo, W., Enhancement of charge transfer between graphene and donor-pi-acceptor molecule for ultrahigh sensing performance. *Nanoscale* **2017**, *9* (42), 16273-16280.
10. Huder, L.; Rinfrey, C.; Rouchon, D.; Benayad, A.; Baraket, M.; Izzet, G.; Lipp-Bregolin, F.; Lapertot, G.; Dubois, L.; Proust, A.; Jansen, L.; Duclairoir, F., Evidence for Charge Transfer at the Interface between Hybrid Phosphomolybdate and Epitaxial Graphene. *Langmuir* **2016**, *32* (19), 4774-83.
11. Fan, S.; Tang, X.; Zhang, D.; Hu, X.; Liu, J.; Yang, L.; Su, J., Ambipolar and n/p-type conduction enhancement of two-dimensional materials by surface charge transfer doping. *Nanoscale* **2019**, *11* (32), 15359-15366.
12. Gao, J.; Tong, M.; Xing, Z.; Jin, Q.; Zhou, J.; Chen, L.; Xu, H.; Li, G., A covalently linked dual network structure achieved by rapid grafting of poly(p-phenylenediamine)-phosphomolybdic acid on reduced graphene oxide aerogel for improving the performance of supercapacitors. *Chem Commun (Camb)* **2020**, *56* (53), 7305-7308.
13. Giangregorio, M. M.; Jiao, W.; Bianco, G. V.; Capezzuto, P.; Brown, A. S.; Bruno, G.; Losurdo, M., Insights into the effects of metal nanostructuring and oxidation on the work function and charge transfer of metal/graphene hybrids. *Nanoscale* **2015**, *7* (30), 12868-77.
14. Coros, M.; Varodi, C.; Pogacean, F.; Gal, E.; Pruneanu, S. M., Nitrogen-Doped Graphene: The Influence of Doping Level on the Charge-Transfer Resistance and Apparent Heterogeneous Electron Transfer Rate. *Sensors (Basel)* **2020**, *20* (7).
15. Pham, C. V.; Repp, S.; Thomann, R.; Krueger, M.; Weber, S.; Erdem, E., Charge transfer and surface defect healing within ZnO nanoparticle decorated graphene hybrid materials. *Nanoscale* **2016**, *8* (18), 9682-7.

16. Xu, J.; Cao, X.; Xia, J.; Gong, S.; Wang, Z.; Lu, L., Phosphomolybdic acid functionalized graphene loading copper nanoparticles modified electrodes for non-enzymatic electrochemical sensing of glucose. *Anal Chim Acta* **2016**, *934*, 44-51.
17. Yu, M. A.; Feng, Y.; Gao, L.; Lin, S., Phosphomolybdic acid supported single-metal-atom catalysis in CO oxidation: first-principles calculations. *Phys Chem Chem Phys* **2018**, *20* (31), 20661-20668.
18. Qiu, G.; Xiao, Q.; Hu, Y.; Qin, W.; Wang, D., Theoretical study of the surface energy and electronic structure of pyrite FeS<sub>2</sub> (100) using a total-energy pseudopotential method, CASTEP. *J Colloid Interface Sci* **2004**, *270* (1), 127-32.
19. Grimme, S., Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comput Chem* **2006**, *27* (15), 1787-99.
20. Korth, M.; Thiel, W., Benchmarking Semiempirical Methods for Thermochemistry, Kinetics, and Noncovalent Interactions: OMx Methods Are Almost As Accurate and Robust As DFT-GGA Methods for Organic Molecules. *J Chem Theory Comput* **2011**, *7* (9), 2929-36.

# Figures

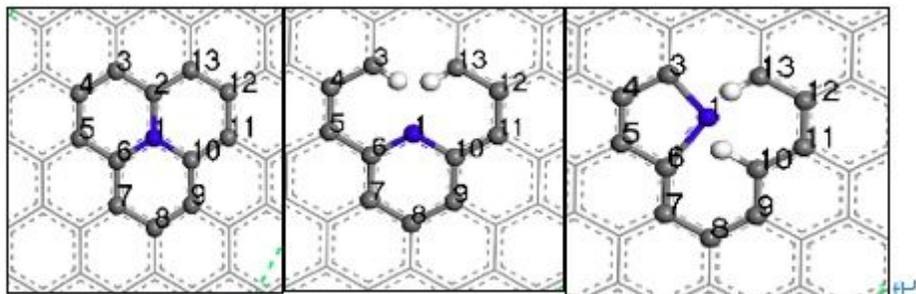


Figure 1

the models of three types nitrogen doped graphene (left A, center B, right C)

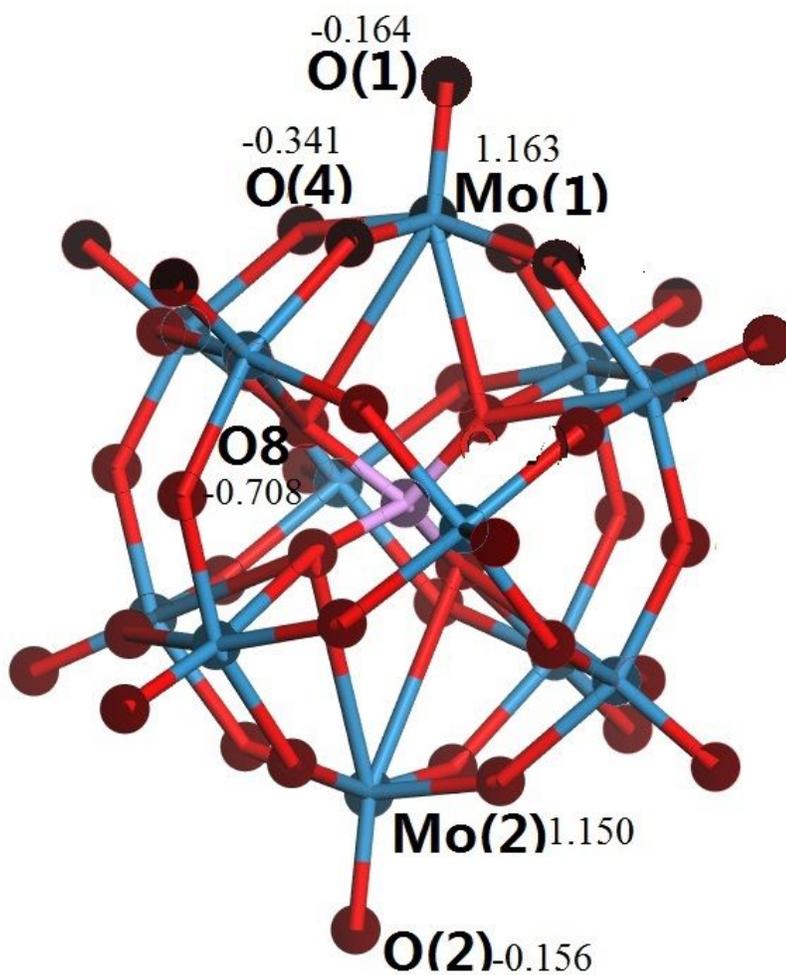
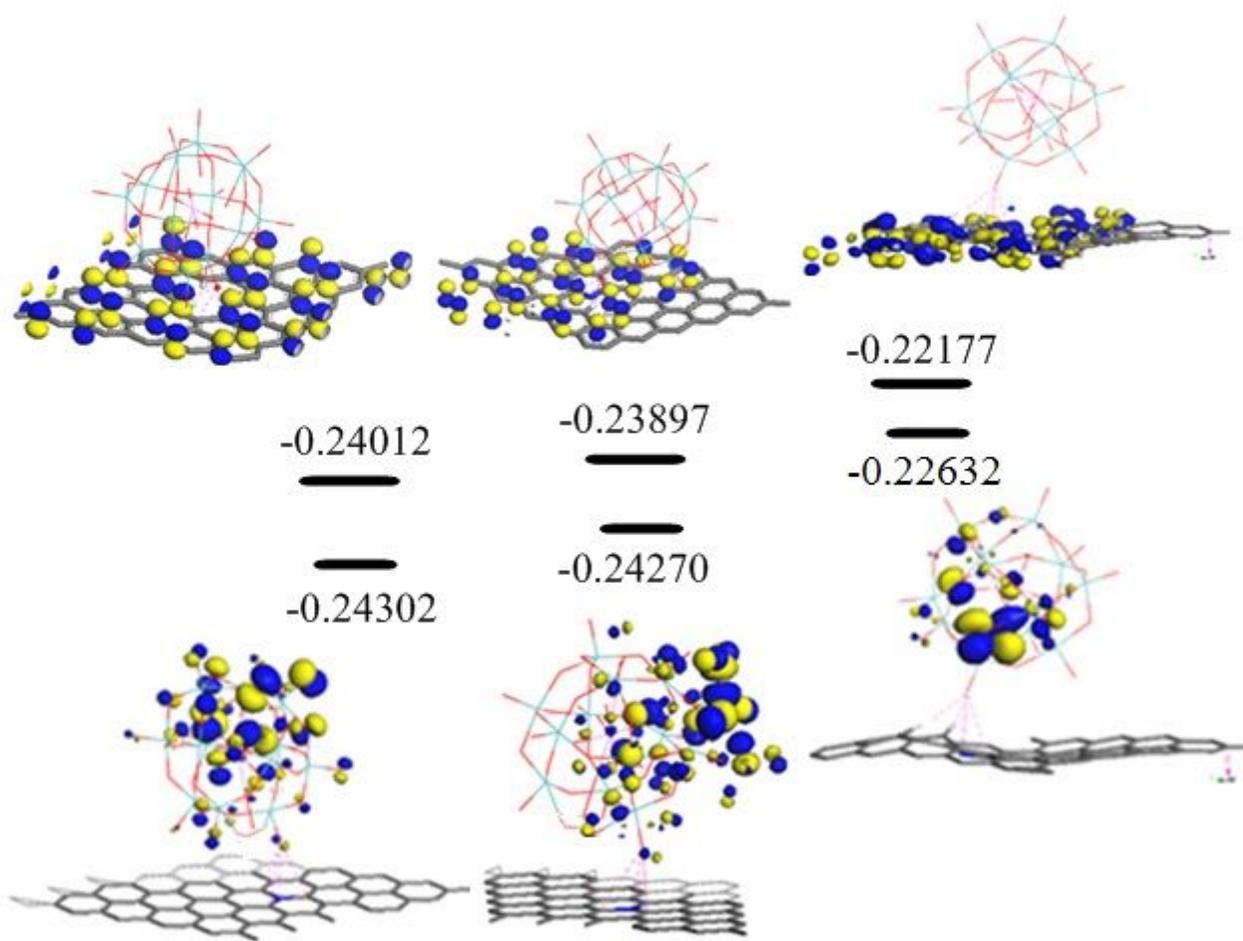


Figure 2

The structure of PMA



**Figure 3**

the frontier orbital distribution of three composite3

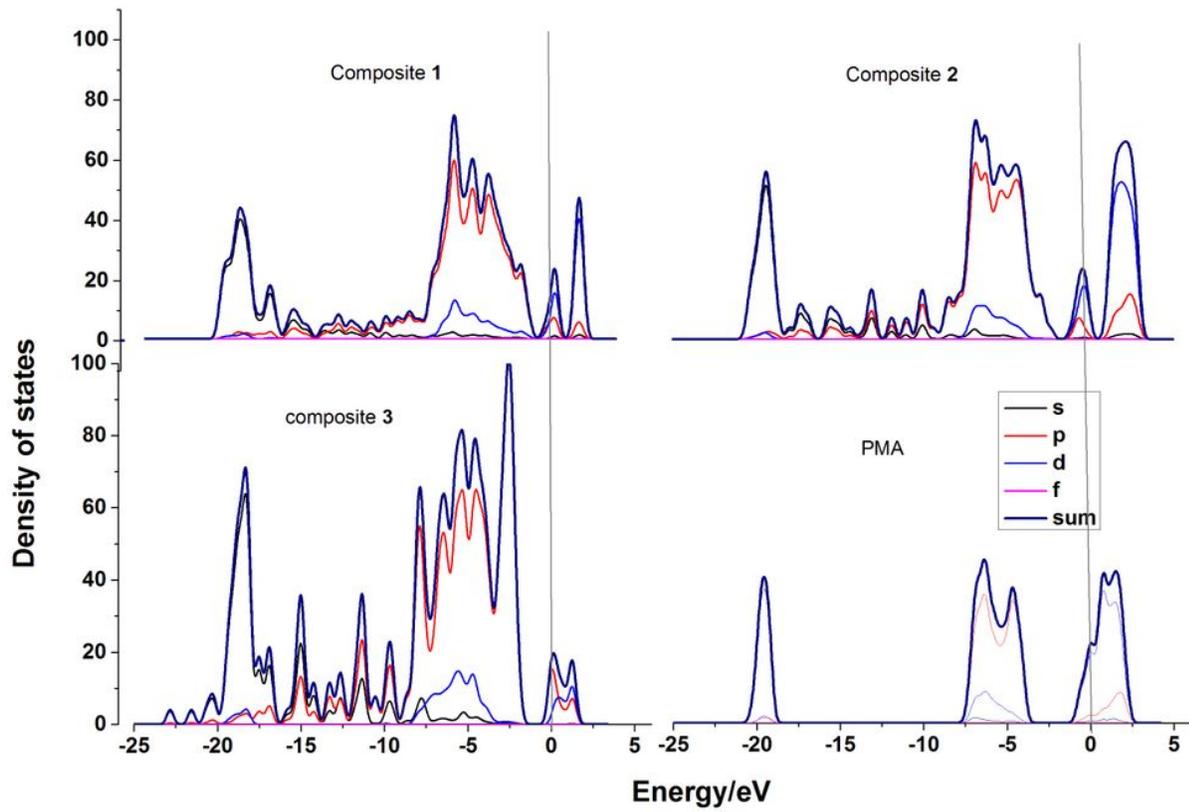


Figure 4

the density of states for three composites and PMA