

The Oxygen Reduction Activity of Nitrogen-doped Graphene

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Graphite nitrogen, pyridine nitrogen and pyrrole nitrogen are the main nitrogen types in nitrogen-doped graphene materials. In order to investigate the mechanism of the oxygen reduction activity of nitrogen-doped graphene, several models of nitrogen-doped graphene with different nitrogen contents and different nitrogen types are developed. The nitrogen content is varied from 1.3 at% to 7.8 at%, and the adsorption energy is calculated according to the established models, then the band gaps are analyzed through the optimization results, so as to compare the magnitude of the conductivity. Finally, the oxygen reduction activity of graphite nitrogen-doped graphene (GNG) is found to be better than pyridine nitrogen-doped graphene (PDNG) and pyrrole nitrogen-doped graphene (PLNG) when the nitrogen content is lower than 2.6 at%, and the oxygen reduction activity of PDNG is the best when the nitrogen content was higher than 2.6 at%.

Keywords: Nitrogen Doping; Graphene; Oxygen Reduction Activity; Molecular Simulation.

INTRODUCTION

With the development of science and technology, advanced materials are receiving more and more attention. The new carbon material-graphene has brought about a new research upsurge with its excellent structural characteristics and properties¹. Graphene shows unique electrical properties, has excellent oxygen reduction activity as the catalyst support and has promising applications in the field of catalysis².

The regular structure and semiconductor properties of graphene limit its regulated space, so the effective properties of graphene performance can be improved by introducing other elements through chemical doping. At the same time, heteroatomic doped carbon catalysts can improve its ORR activity and chemical stability³. Chemical doping can also change the internal structure of graphene, e.g. doping with nitrogen, boron, phosphorus and other elements, in which nitrogen doping can effectively improve the oxygen reduction activity of graphene⁴. The most common nitrogen-doped graphene can be divided into graphite nitrogen-doped graphene (GNG), pyridine nitrogen-doped graphene (PDNG)⁵ and pyrrole nitrogen-doped graphene (PLNG)⁶. GNG is doped by replacing carbon atoms in the plane of graphene. PDNG and PLNG are also doped by replacing carbon atoms that are unsaturated with carbon defects, but the final form of doping of PDNG was a five-membered ring⁷. The influence of different types of nitrogen doping on the oxygen reduction activity of graphene is still controversial. It has been suggested that GNG is the main reason for the improvement of oxygen reduction activity, but it has been suggested that PDNG and PLNG can also improve the oxygen reduction activity of graphene⁶⁻⁸. Weththasinha H et al.⁹ prepared nitrogen-doped lotus stem carbon (N-LSC) with nitrogen doping content of 6.5 at% through experiments, which was proved to be comparable to platinum-based catalysts due to its high pyridine nitrogen content and porous structure. Haile A S et al.¹⁰ proved that pyridinic N-doped graphene of Co substrate had a higher overpotential than Graphitic N-doped graphene. Sanchez-Padilla N M et al.¹¹ experimentally proved that introducing pyridine nitrogen and

pyrrole nitrogen into the carbon lattice can improve the activity of the catalyst. However, the nitrogen content in nitrogen-doped graphene was different in different studies, and it is speculated that the different conclusions maybe due to the different nitrogen contents. And most researchers have only studied the effects of GNG and PDNG on oxygen reduction reaction. Therefore, the oxygen reduction activities of nitrogen-doped graphene with different nitrogen contents are studied, and the effects of GNG, PDNG and PLNG on the oxygen reduction activities of graphene are researched respectively.

Directly experimental research requires more time, and cannot reach the ideal experimental conditions. With the maturity of computer technology, computer simulations are not only inexpensive but also more convenient and reliable, provided they are used wisely. Materials Studio software is an effective tool to study the structure and properties of atomic-level carbon materials. It is easy to build and study molecular models, as well as to install and operate. It has low cost. The CASTEP modules in the software adopt the leading simulation methods in LDA and GGA. The analysis of energy band structure and the calculation of adsorption energy are also very effective¹². So, this paper uses Materials Studio software to build a model of nitrogen-doped graphene with different nitrogen contents, to calculate the nitrogen-doped graphene by CASTEP modules.

MODELING AND CALCULATION METHOD

Establishment of mode

Graphene is a two-dimensional crystal structure of a single atomic layer composed of six hybrid carbon atoms, therefore Materials Studio software is used to establish a periodic flat plate model. The “graphite“ in the template library is used as a repeating unit to establish a supercell of $6 \times 5 \times 1$ with a total of 77 carbon atoms. Considering the interaction between mirrors, the vacuum layer is taken to be 15 Å. In order to make the observation of the model more intuitive and convenient, the lattice parameters are changed. The length and azimuth of the crystal frame were adjusted so that

both the crystal frame and the model are changed from oblique hexahedron to rectangle. It is difficult to mix graphite nitrogen, pyridine nitrogen and pyrrole nitrogen individually in the experiment, so it is hard to compare their respective effects on the oxygen reduction activity of graphene. Besides, only one nitrogen doping can be used in the simulation calculation to achieve the best simulation conditions.

Hence, only three nitrogen-doped graphene models with doped graphite nitrogen, pyridine nitrogen and pyrrole nitrogen are established, and each nitrogen-doped graphene model is further doped with 1, 2, 3, 4, 5, 6 nitrogen atoms to form nitrogen-doped graphene models with nitrogen contents of 1.3 at%, 2.6 at%, 3.9 at%, 5.2 at%, 6.5 at%, 7.8 at%, respectively, as shown in Figure 1. In order to ensure the randomness of each

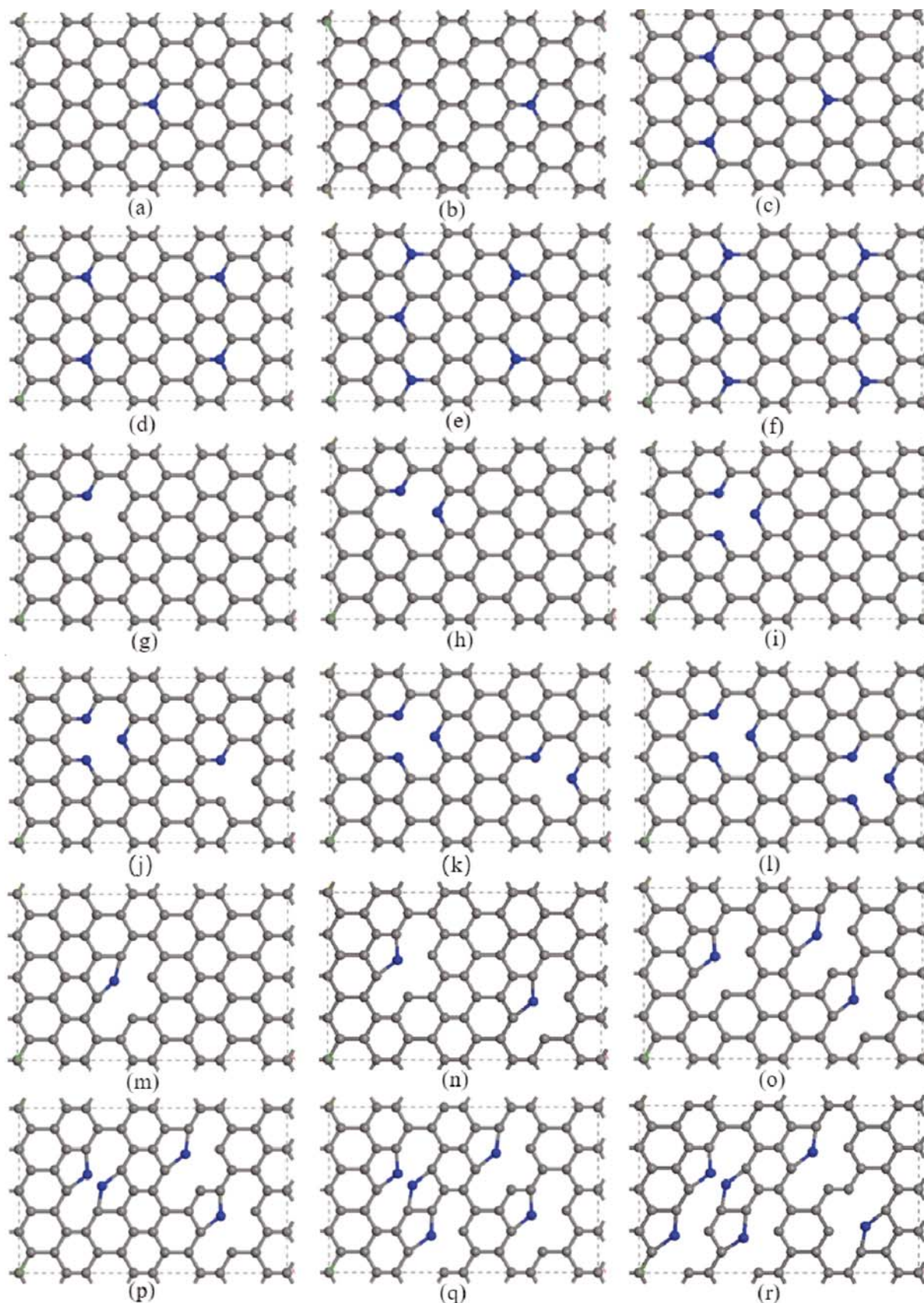


Figure 1. Structure of nitrogen-doped graphene GNG (a ~f), PDNG (g ~f) and PLNG (m ~f) with different nitrogen content

nitrogen atom doping, the interval between nitrogen atoms is as average as possible, and the system energy of each configuration is as low as possible.

Calculation method

This paper applies Materials Studio software to carry out all simulation calculations based on the first principles of density functional theory. The structure of the established nitrogen-doped graphene model is optimized using the CASTEP module of Materials Studio software. The geometric optimization is chosen as the task goal, and the generalized gradient approximation theory (GGA-PBE) exchanged correlation functional method is used for the simulation calculation. Since the whole nitrogen-doped graphene model is a dense architecture, the results obtained by this method are more accurate¹³. The simulations are based on the following parameters: the corresponding cutoff energy is 400 eV, the convergence mass is medium, the convergence accuracy of the total energy is 2.0×10^{-5} eV/Å, the maximum force per atom is 0.05 eV/Å, the maximum displacement is 0.002 Å, the maximum number of iteration steps is 100, considering the spin polarization effect, the normal spin is used as the initial spin. The Brillouin zone integral adopts Monkhorst-Pack mesh, and the K point value is $2 \times 2 \times 1$. To compare the band gap and adsorption energy of the nitrogen-doped model system with nitrogen contents of 1.3 at%~7.8 at% respectively, the band structure, density of states and layout analysis are selected for operation.

Materials Studio software is an effective tool to study the structural and properties of atomic-level porous materials, providing a comprehensive simulation environment which integrates quantum mechanics, molecular mechanics and mesoscopic simulation. It can solve some important problems in materials and chemical fields such as catalysts, chemical reactions, etc. The CASTEP module has a unique quantum mechanical program based on density functional theory (DFT) that can be used to study homogeneous catalysis, heterogeneous catalysis, molecular reactions, etc. The numerical function of the atomic center grid is employed as atomic base, and the basis function of the atom is obtained through the DFT equation of different atoms so that the system can be accurately described¹⁴. Since the CASTEP module is highly efficient and accurate, it becomes one of the most accurate methods for molecular DFT calculation (especially periodic molecules).

RESULTS AND DISCUSSION

Adsorption

Theoretical and experimental studies show that adsorption energy is an effective description, the relationship between adsorption energy and oxygen reduction activity is of great significance to the performance of catalysts. Adsorption energy is a fundamental parameter for characterizing electrochemical coupling, while the oxygen reduction activity is attributed to interfacial electron coupling. Hence, the adsorption energy is also a good screening factor for defining the oxygen reduction activity of surface reactants. The surface activity of solid catalysts is determined by the overall activity (intrinsic) of

each active site and the number of exposed active sites (extrinsic), while the electrocatalytic oxygen reduction process contains the adsorption process of the surface reactants, breaking some binding bonds between reactants and catalysts to form new chemical bonds and obtain active intermediates¹⁵.

As nitrogen-doped graphene adsorbs oxygen molecules, there will be physical and chemical adsorption. The system is relaxed by GGA-PW91 method to obtain the stable configuration of adsorbed oxygen molecules, and then the related properties of adsorbed oxygen in each system are analyzed separately. The adsorption energy ($E_{\text{adsorption}}$) of the system is defined as follows:

$$E_{\text{adsorption}} = E_{\text{total}} - (E_{\text{molecule}} + E_{\text{surface}})$$

In the nitrogen-doped graphene adsorption oxygen model, the energy of oxygen molecules is E_{molecule} , the energy of different nitrogen-doped graphene is E_{surface} , and the total energy of the system is E_{total} , that is the sum of the energy of oxygen molecules and the energy of nitrogen-doped graphene. The adsorption energy reflects the strength of the material interaction on both sides of the interface. If the adsorption energy is negative, the greater the absolute value, the greater the interaction force.

When physically adsorbed, oxygen molecules will adsorb over the parallel sky of the nitrogen-doped graphene substrate, so the energy of the whole system is lower and the structure is more stable. Oxygen molecules will have vacancy adsorption (oxygen molecules are located directly above the carbon ring), bridge adsorption (carbon-carbon bond or carbon-nitrogen bond is directly above) and top adsorption (nitrogen or carbon atom is directly above). However, the oxygen molecules on the surface of nitrogen-doped graphene prefer top adsorption, one of the oxygen atoms adsorbs above the nitrogen atom when nitrogen is doped⁵. Therefore, based on the above characteristics of oxygen adsorption by nitrogen-doped graphene, a model was established and optimized, and the final model of oxygen molecule adsorption on graphene is shown in Figure 2 (a), the model of oxygen molecule adsorption on GNG is shown in Figure 2 (b), the model of oxygen molecule adsorption on PDNG is shown in Figure 2 (c), and the model of oxygen molecule adsorption on PLNG is shown in Figure 2 (d). It can be seen from the figure that when oxygen molecules are adsorbed on different graphene surfaces, and its bond length, distance and position from the graphene surface will change, indicating that the adsorption of oxygen molecules by different graphene is different.

After simulation calculation, adsorption energy of physically adsorbed oxygen molecules and bond length of oxygen molecules by GNG, PDNG and PLNG with different nitrogen contents are shown in Table 1. The table shows that the adsorption energy of graphene doped with nitrogen increases significantly when the nitrogen content ranges from 0 at% to 1.3 at%, indicating that nitrogen doping can improve the adsorption performance of graphene. Comparing the adsorption energy of GNG, PDNG and PLNG when the nitrogen content is the same, it is found that the adsorption energy of GNG is the largest, indicating that the doping of graphite nitrogen has the most obvious effect on the adsorption

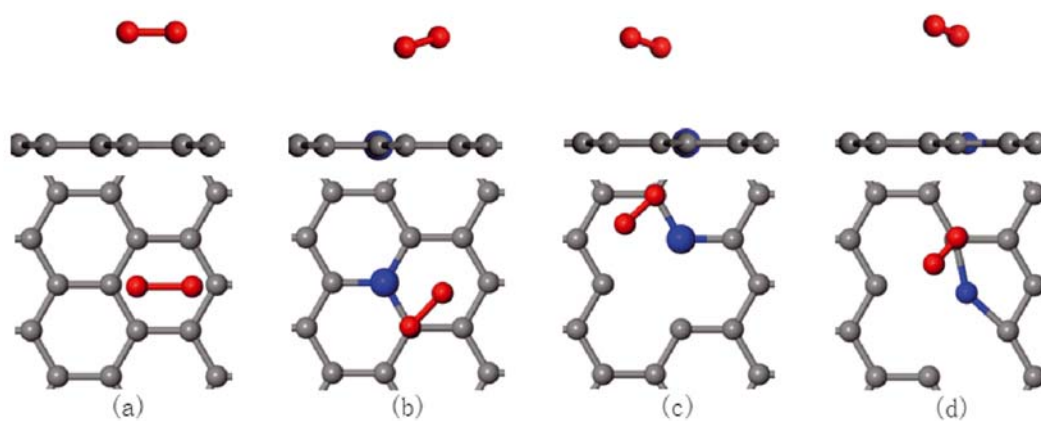


Figure 2. Stable physical adsorption structure of oxygen molecules on graphene (a), GNG (b), PDNG (c) and PLNG (d)

performance of graphene. This is because the binding strength of oxygen and graphene is closely related to the electron contribution of graphene to oxygen, and each graphite nitrogen doping will introduce an extra electron to graphene, thus promoting the binding and adsorption of oxygen, and further improving the ORR activity¹⁶. The respective adsorption energies of GNG, PDNG and PLNG are almost the same with different nitrogen contents, which indicates that the different nitrogen contents have little effect on the adsorption performance of graphene. This is probably due to the greater distance between the doped nitrogen atoms and the lesser effect of graphene on the adsorption of oxygen molecules. The longer the bond length of the O-O indicates that the stronger the adsorption of oxygen by graphene, so the comparison of O-O bond length can also prove the above view.

When chemical adsorption occurs, oxygen molecules are chemically adsorbed and bonded with carbon atoms connected to nitrogen atoms in nitrogen-doped graphene. Besides, they are adsorbed on the graphene surface in the structure form of OOH, O and OH¹⁷ because the OOH adsorption form is the most common and therefore one

of the OOH adsorption forms is selected, as shown in Figure 3. As can be seen from the figure, the types of nitrogen doping is different, thus the bond length of C-O and the change of position of nitrogen atoms connected to oxygen molecules are also different. The specific adsorption energy and C-O bond length can be seen in Table 2. When the nitrogen content increases gradually, the adsorption energy also increases significantly; when the nitrogen content is the same, the adsorption energy of GNG is the largest; the adsorption energy of GNG, PDNG and PLNG with different nitrogen contents is not much different. It can be seen that when nitrogen-doped graphene adsorbs oxygen molecules, the conclusion of chemical adsorption is basically consistent with that of physical adsorption.

Conductivity

Conductivity is another effective parameter to describe the oxygen reduction activity of the catalyst, while the band gap is the difference between the lowest point of the conduction band and the highest point of the valence band. The larger the band gap, the harder it is to excite electrons from the valence band to the conduction band,

Table 1. Related properties of physical adsorption of oxygen by GNG, PDNG and PLNG with different nitrogen contents

Nitrogen content		0 at%	1.3 at%	2.6 at%	3.9 at%	5.2 at%	6.5 at%	7.8 at%
Adsorption energy (eV)	G NG	0.142	0.301	0.307	0.309	0.308	0.304	0.302
	P DNG		0.218	0.221	0.222	0.221	0.220	0.221
	P LNG		0.192	0.195	0.194	0.192	0.193	0.191
O-O bond length (Å)	G NG	1.253	1.268	1.271	1.273	1.272	1.269	1.269
	P DNG		1.261	1.263	1.263	1.260	1.261	1.260
	P LNG		1.258	1.259	1.261	1.259	1.259	1.258

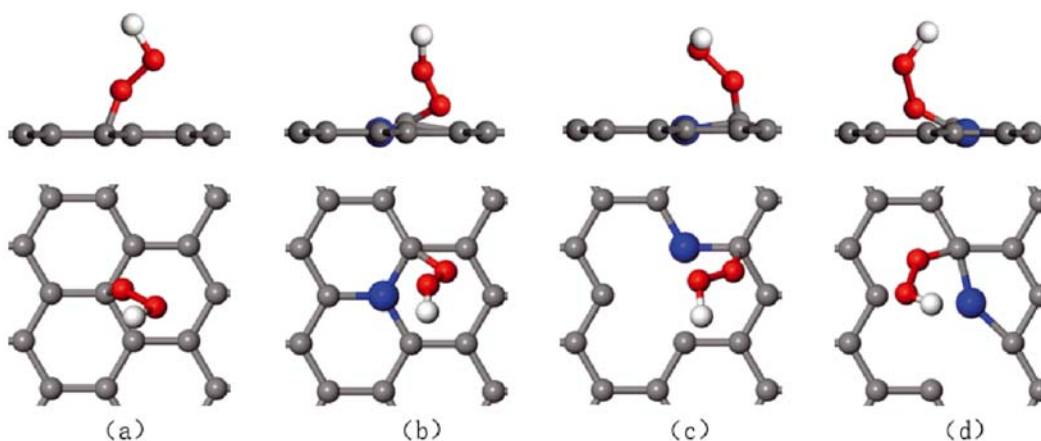
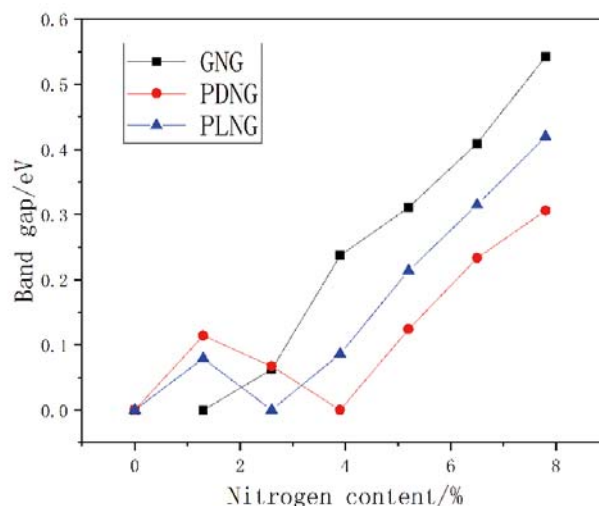


Figure 3. Stable chemisorption structure of oxygen molecules on graphene (a), GNG (b), PDNG (c) and PLNG (d)

Table 2. Related properties of chemical adsorption of oxygen by GNG, PDNG and PLNG with different nitrogen contents

Nitrogen content		0 at%	1.3 at%	2.6 at%	3.9 at%	5.2 at%	6.5 at%	7.8 at%
Adsorption energy (eV)	G NG	2.642	3.411	3.434	3.449	3.434	3.455	3.452
	P DNG		3.137	3.167	3.186	3.170	3.156	3.161
	P LNG		2.955	2.964	2.957	2.991	2.963	2.955
C-O bond length (Å)	G NG	1.415	1.325	1.323	1.324	1.322	1.321	1.323
	P DNG		1.367	1.366	1.364	1.365	1.367	1.365
	P LNG		1.378	1.377	1.377	1.376	1.376	1.377

then the lower the intrinsic carrier concentration and the lower the conductivity¹⁸. The band gaps of the different nitrogen contents of GNG, PDNG and PLNG are shown in Table 3, and the electrical conductivity can be judged according to the band gap. To more intuitively observe the trend of the band gap of GNG, PDNG and PLNG with different nitrogen contents, a broken line diagram is made according to Table 3 as shown in Figure 4. It can be seen from the figure that the band gap of the GNG increases gradually with the increase of nitrogen content, while the band gap of both PDNG and PLNG increases first and then decreases and then increases. The GNG band gap has been increased because nitrogen doping destroys the delocalized π bond around the N atoms, thus destroying the semiconductor structure of graphene and producing band gap, which makes the conductivity decrease; when the nitrogen content is 1.3 at%, it is not enough to destroy the semiconductor structure of graphene because the nitrogen content is too low. The overall trend of band gap of PDNG and PLNG is also larger gradually due to the destruction of graphene structure by nitrogen doping. However, when the nitrogen content is 1.3 at% ~ 3.9 at% and 1.3 at% ~ 2.6 at%, the band gap of PDNG and PLNG is becoming smaller. Because PDNG and PLNG are doped in the way of replacing the unsatisfied carbon atom with the carbon defect, the carbon defect will also affect the semiconductor structure of graphene. Nevertheless, pyridine nitrogen and pyrrole nitrogen can reduce the influence of N atom on the conductivity of graphene. Therefore, when the nitrogen content is 1.3 at% ~ 3.9 at% and 1.3 at% ~ 2.6 at%, the influence of pyridine nitrogen and pyrrole nitrogen on the conductivity of graphene is greater than carbon defect. When the nitrogen content is higher than 2.6 at%, the band gap of GNG is greater than that of PLNG and PDNG which also shows that pyridine nitrogen and pyrrole nitrogen can reduce the effect of nitrogen doping on the conductivity of graphene. When the nitrogen content is less than 3.9 at%, the band gap of PLNG is smaller than that of PDNG, which may be because the effect of pyrrole nitrogen on the conductivity of graphene is more obvious. But when the nitrogen content is higher than 3.9 at%, PLNG has more carbon defects than PDNG, so the nitrogen defects of PLNG have a more obvious effect on the conductivity of graphene, and the higher nitrogen content is, the more nitrogen defects there are, therefore, the band gap of PLNG is larger than PDNG.

**Figure 4.** The band gap of GNG, PDNG and PLNG with different nitrogen contents

CONCLUSION

The adsorption energy and conductivity of GNG, PDNG and PLNG with different nitrogen contents are investigated based on density functional theory simulations. The effects of doping graphite nitrogen, pyridine nitrogen and pyrrole nitrogen in graphene are then compared. Based on the simulation results, nitrogen doping can significantly increase the adsorption energy of graphene from both physical and chemical adsorption energy. The adsorption energy of GNG with different nitrogen contents is always greater than that of PDNG and PLNG, and the difference of nitrogen content has little effect on the adsorption energy. In terms of conductivity, when the nitrogen content is less than 2.6 at%, the conductivity of GNG is the best; when the nitrogen content is more than 2.6 at%, the conductivity of PDNG is better than that of GNG and PLNG. Besides, both PDNG and PLNG can effectively reduce the effect of nitrogen doping on graphene conductivity. Considering adsorption energy and conductivity, when nitrogen content is lower than 2.6 at%, the adsorption energy and conductivity of GNG are better than PDNG and PLNG, so the oxygen reduction activity of GNG is better than PDNG and PLNG; when the nitrogen content is higher than 2.6 at%, the difference of conductivity becomes larger, and the influence of conductivity on the oxygen reduction activity is greater than that of adsorption energy, so PDNG has the best oxygen reduction activity.

Table 3. The band gap of GNG, PDNG and PLNG with different nitrogen contents

Nitrogen content		0 at%	1.3 at%	2.6 at%	3.9 at%	5.2 at%	6.5 at%	7.8 at%
Bandgap (eV)	G NG	0	0	0.062	0.237	0.311	0.409	0.542
	P DNG		0.114	0.067	0	0.124	0.233	0.306
	P LNG		0.079	0	0.156	0.277	0.392	0.490

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